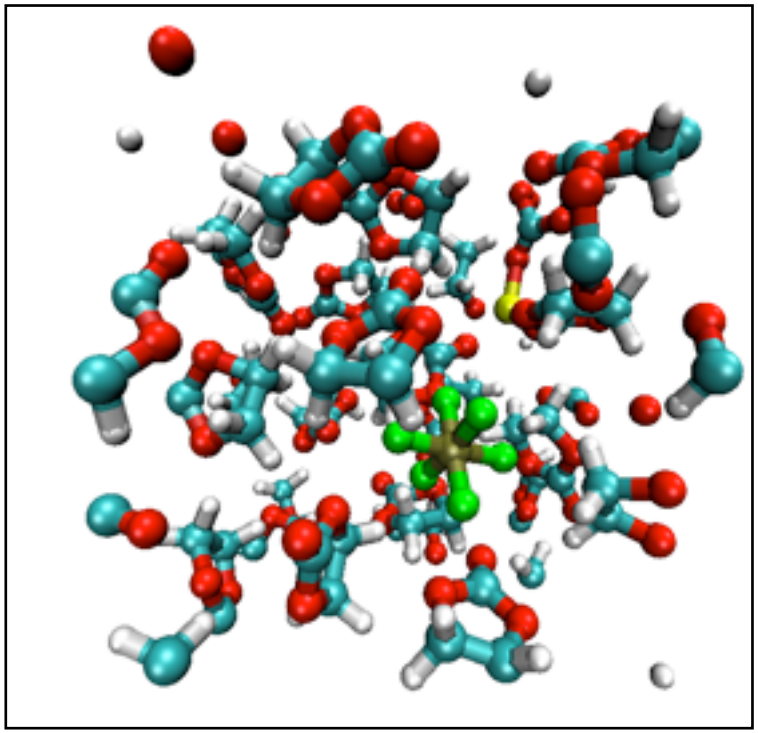
# Properties of Liquid Electrolytes for Li-ion Battery Applications from First Principles Molecular Dynamics



Spontaneous solvation of $LiPF_6$ in Ethylene-Carbonate

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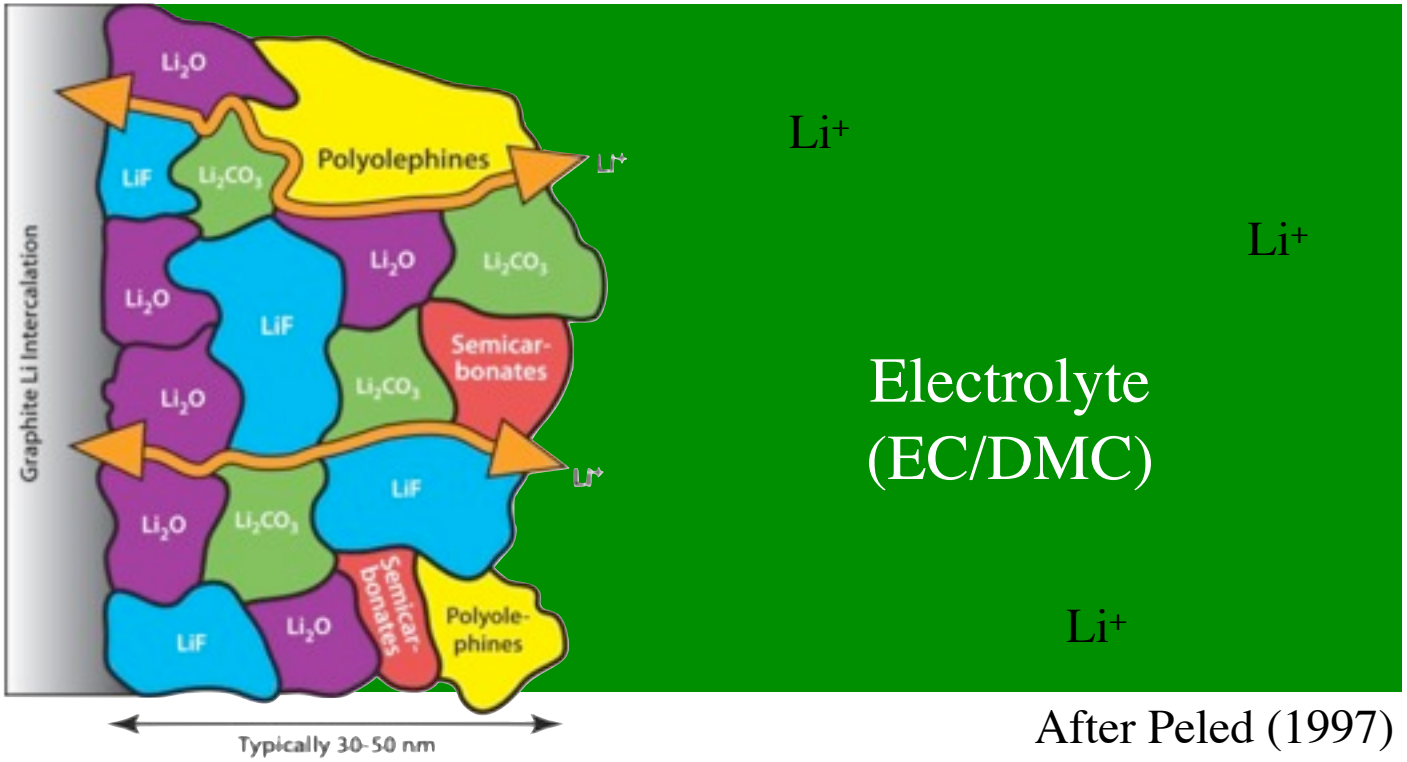
# One of our long term goals

## 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)

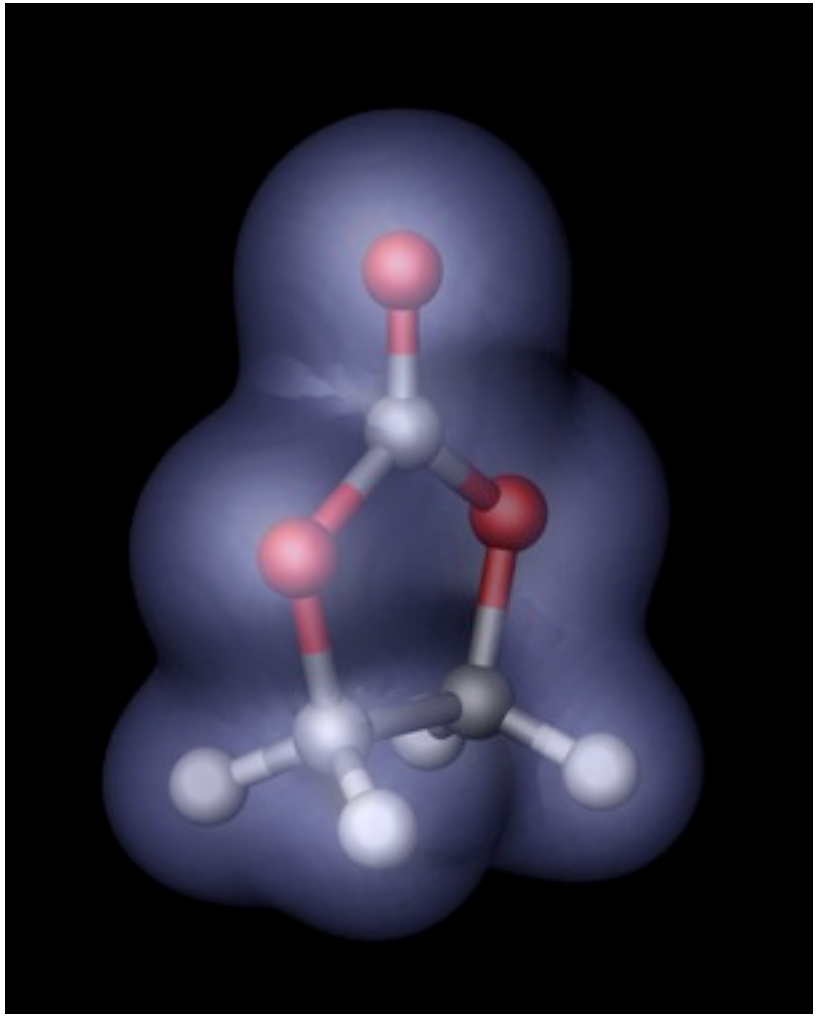
Supercells with 27 EC/PC molecules, 1 $LiPF_6$ (~0.5 M)

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

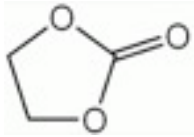


Ethylene carbonate

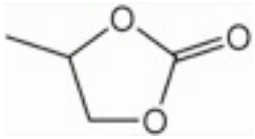
$C_3H_4O_3$

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

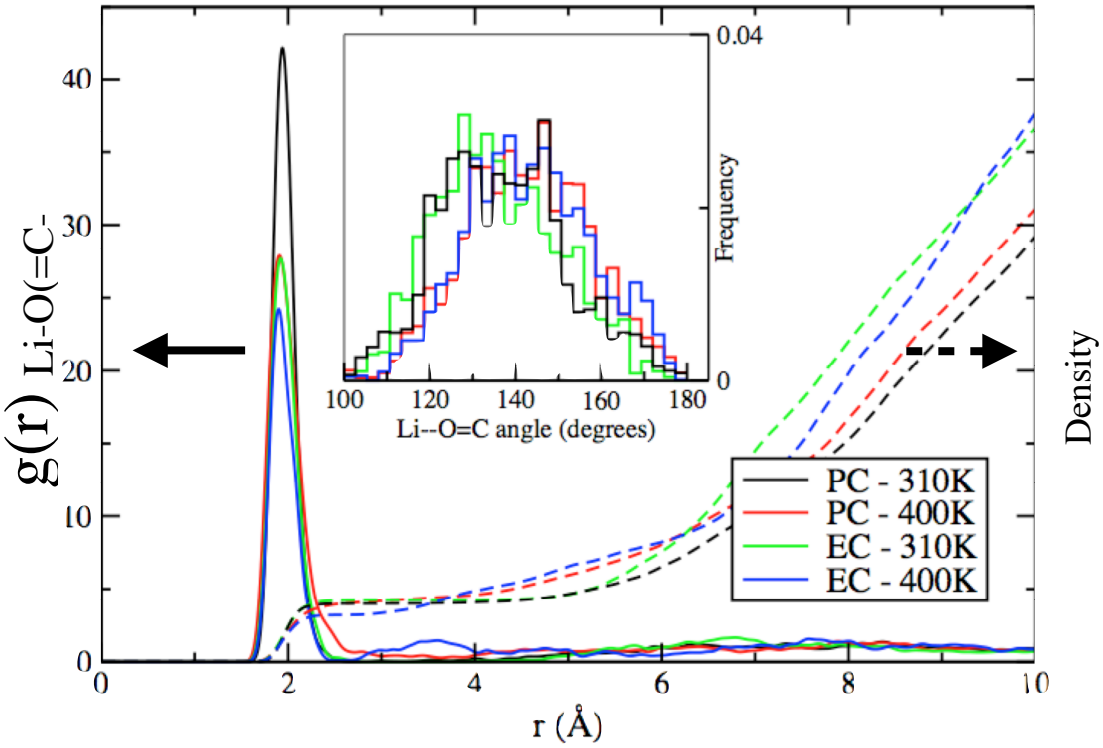
**EC: $C_3H_4O_3$**



**PC: $C_4H_6O_3$**



# Li Partial radial distribution function and coordination number

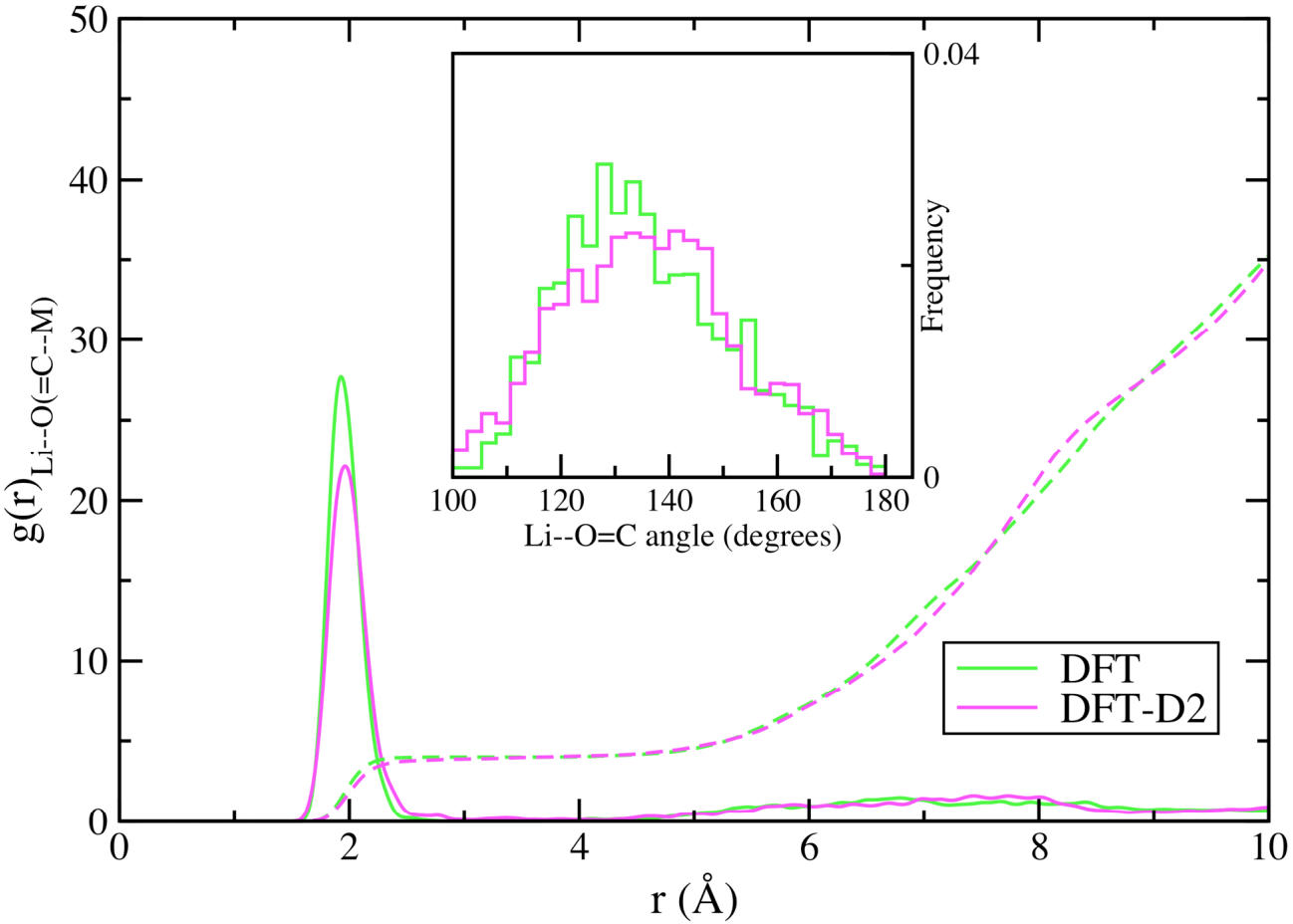



**1st Li solvation shell 4 EC or PC molecules (neutrons: 4.5 at 1.5M, classical: 3.6 EC 298K)**

**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



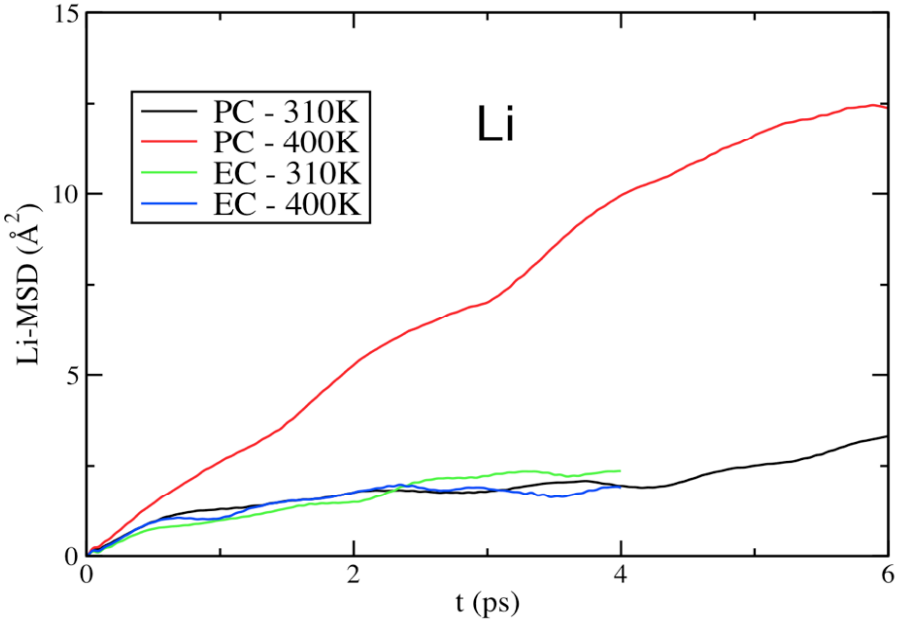

**Grimme's empirical vdw potential (PBE-D2)**

**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)**

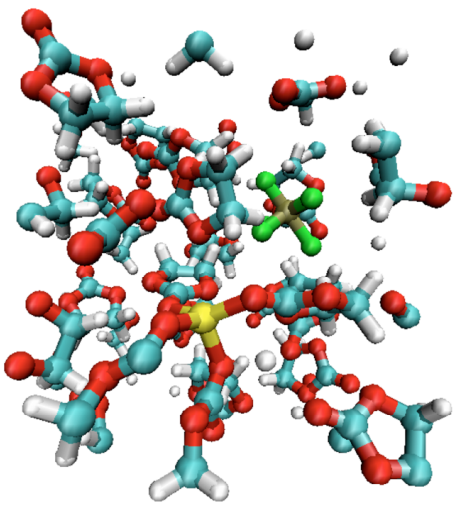
**Calc. ~3.7x10$^{-9}$ m$^2$/s (400K)**

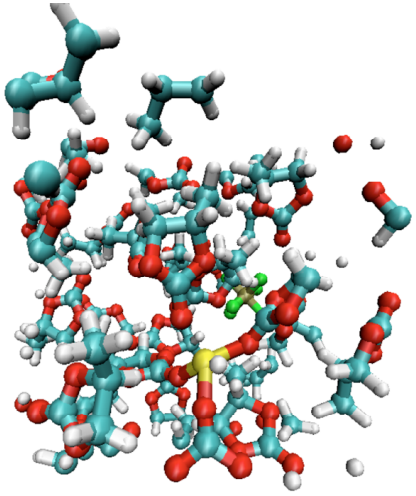
**Expt. ~0.4x10$^{-9}$ m$^2$/s (298K)**

**Nishida ECS Trans. (2008) 6 1**

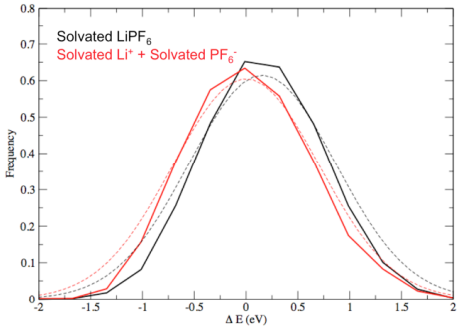
# Rapid solvation of $LiPF_6$ in EC

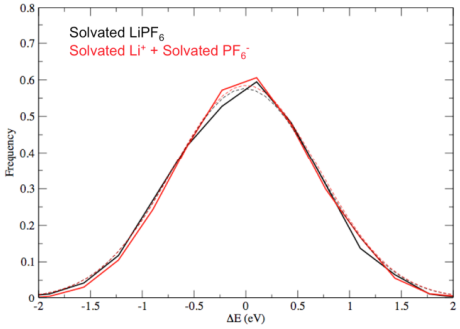
$LiPF_6$/EC





$LiPF_6$/PC

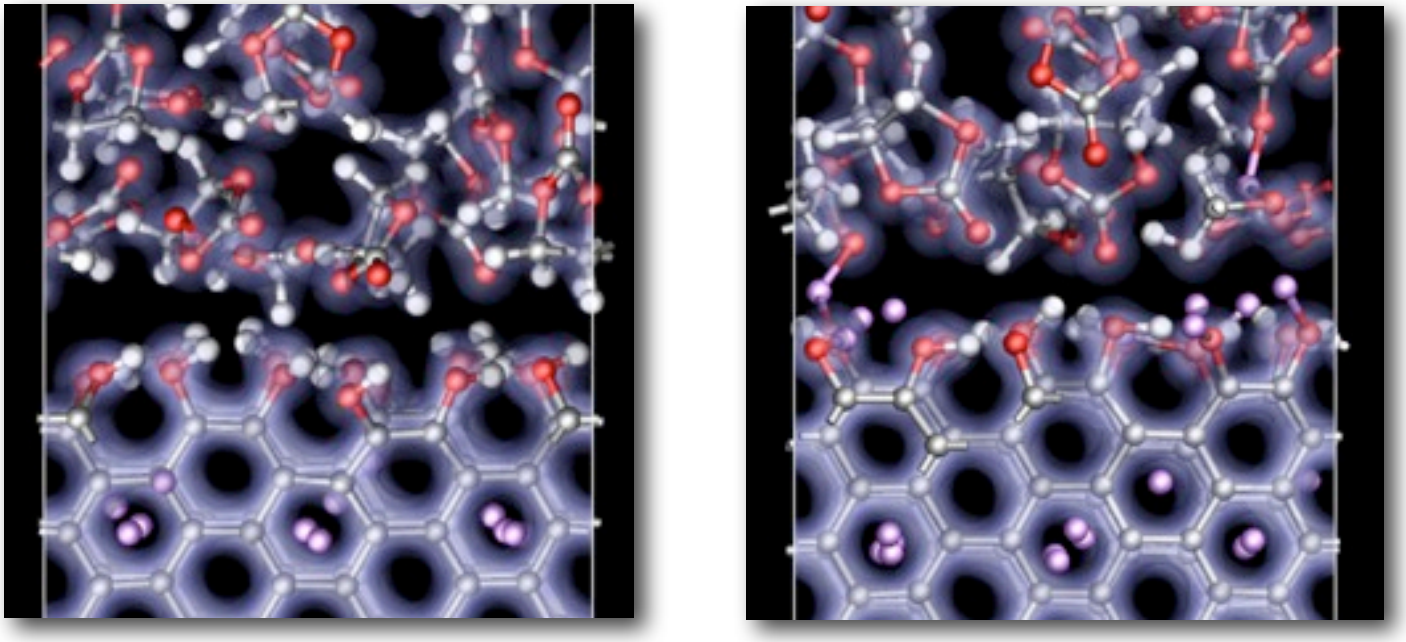



**Li solvation significantly more energetically favourable in EC than PC at 310K**

# Simulations with lithiated carbon anode

Li poor



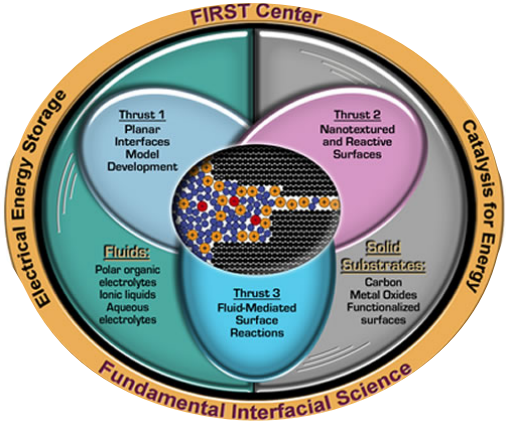
Li rich

- 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

# Summary

P. Ganesh et al. JPCB (ASAP 9 March 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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