LA-SiGMA

Louisiana Alliance for Simulation-Guided Materials Applications

Materials for Energy Storage

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Tulane University

Goals and Milestones

- Recruit and mentor a diverse group of students and postdocs. Progress is described in subsequent reports.

- Simulate pore filling in electrochemical double layer (EDCL) capacitors based on carbon nanotube (CNT) forests; understand the electronics and the role of quantum capacitance (Focus 1).

- Develop algorithms that combine chemistry and physics of H_2 storage (Focus 2).

- Model catalytic processes with new force fields (Focus 3).

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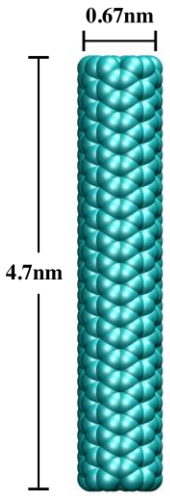
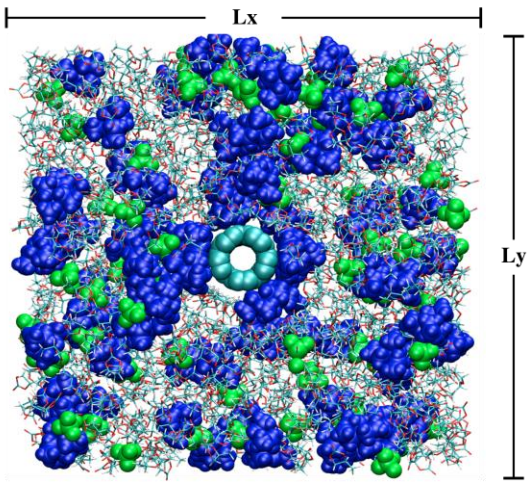
Materials for energy storage





- Focus 1: EDCL supercapacitors based on a CNT forests.
- Focus 2: Optimizing H_2 storage materials utilizing multi-scale modeling.
- Focus 3: Developing new atomic force fields for modeling catalysis.
- New Focus: Improvement of polymer matrix for lithium ion battery performance.

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Molecular modeling of EDCL supercapacitors

- Electrical energy storage where rapid charge/discharge (high power density) is required. Compared to batteries, capacitors have long lifetimes and temperature-insensitivity.
- CNT forests offer possibilities for molecular design. Therefore, a molecular understanding should be worthwhile.
- H. S. Ashbaugh, L. R. Pratt, N. Pesika (Tulane), and S. W. Rick (UNO) combine statistical thermodynamics, *ab initio* molecular dynamics, large scale molecular simulations, and experiments.

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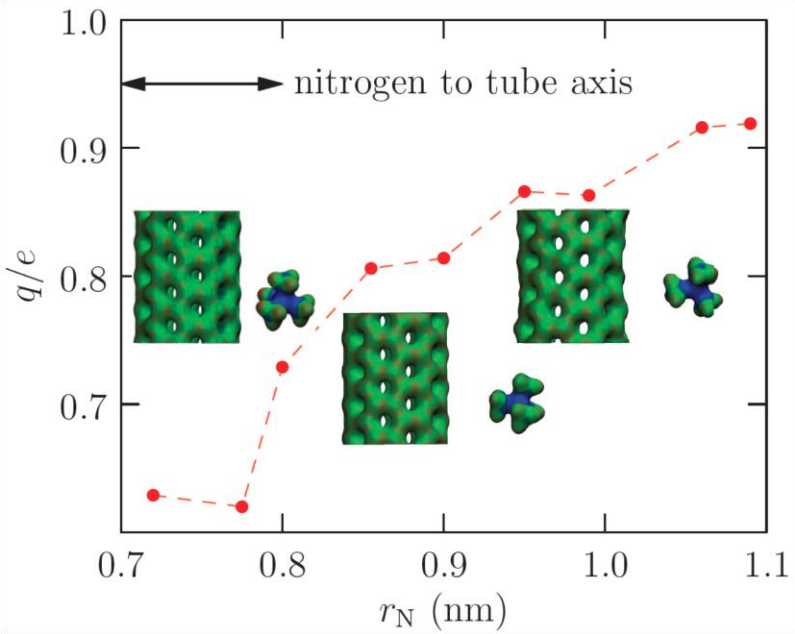
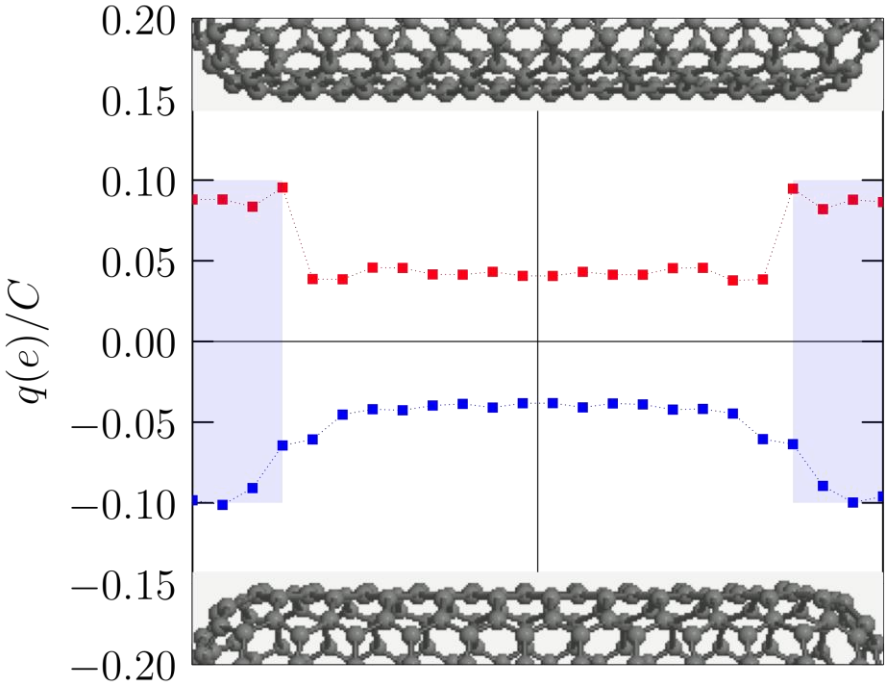
Focus 1

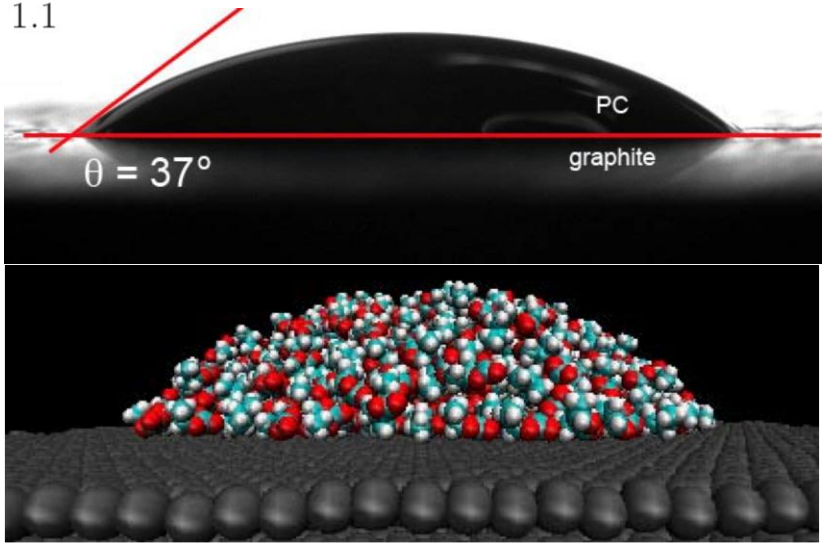
Basics for ECDL/CNT supercapacitors

- Quantum capacitance
- Charge transfer





- Wetting of carbon by propylene carbonate drops.



Focus 1

Accurate prediction of properties of electronic materials

- Rigorous method for accurate, predictive calculations of electronic and transport properties of semiconductors. (**BZW-EF** = Bagayoko, Zhao, and Williams method improved by the work of Ekumar and Franklin)

- Applied to band gaps and other properties of TiO_2, Imp, and $SrTiO_3$, excellent agreement with experimental results.

- BZW-EF permits *ab-initio,* accurate, self-consistent calculations of new materials, and can guide the design of semiconductor materials.

  - See the recently published (online) article on $SrTiO_3$ *In AIP Advances by Kumar, Jarrell, Moreno, and Bagayoko*

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Focus 1

Critical issues for hydrogen storage

- Thermodynamics, kinetics, and energy density, *i.e.,* weight of the storage matrix.
- *Ab initio* (electronic structure) computational methods provide atomic-level materials properties, but not dynamic experimental properties.
- Multiscale approach to link large scale thermodynamic and dynamic properties the molecular level characteristics.

Focus 2

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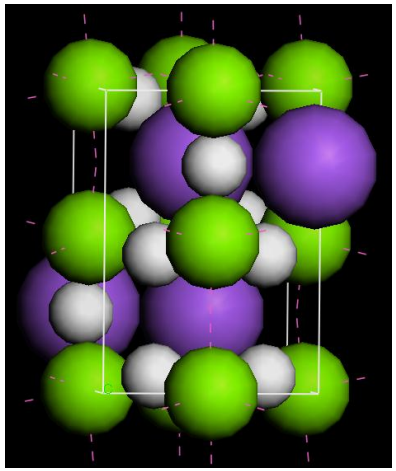
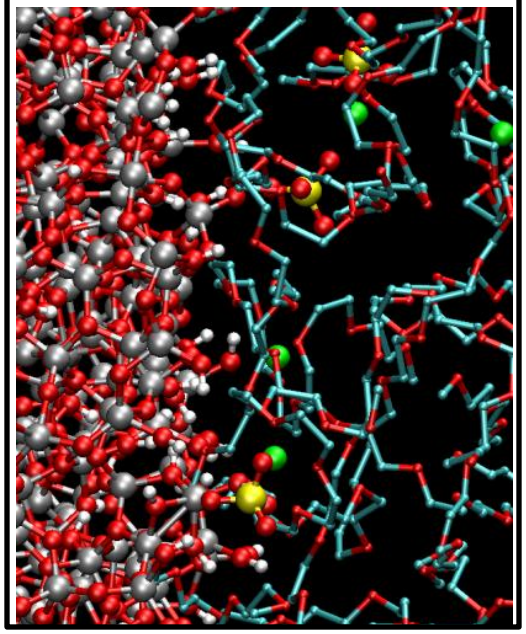
Multi-scale modeling: H_2 storage

Electronic structure calculations / simulations (10s of atoms)



Larger atomic level simulations (1000s of atoms)



Mathematical theory to estimate long time scale dynamics (mesoscale systems)

Compare theoretical results

Experiments on actual systems (mesocale)

Compare simulation results

Use electronic structure for parameterization of atom-based molecular model

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Collaboration spanning multiple disciplines and institutions

Researcher	Institution	Area of Expertise
Daniela Mainardi	LA Tech	Periodic ab initio calculations and dynamics
Les Butler	LSU	Experimental imaging materials in real time
Randy Hall	LSU	Ab initio calculations
Bin Chen	LSU	Force field development and molecular simulation
Weizhong Dai	LA Tech	Mathematical/numerical simulation

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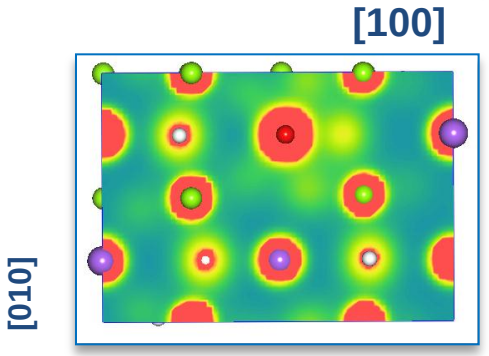
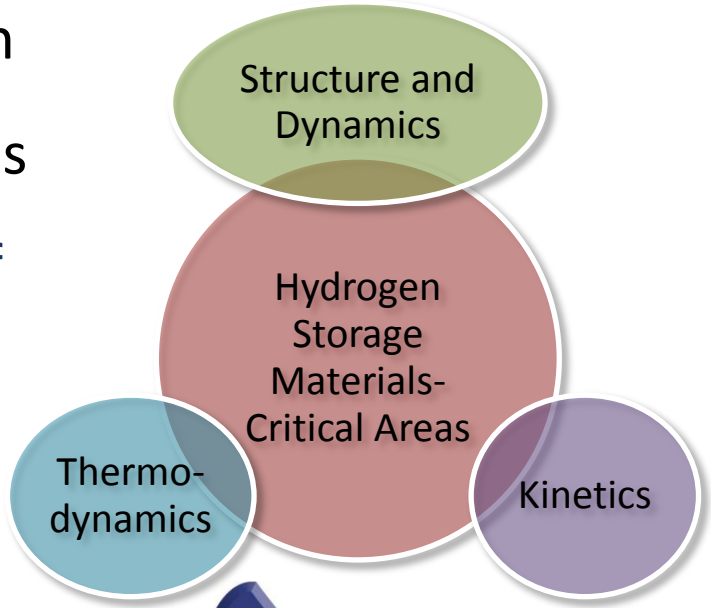
Focus 2

Modeling from *ab-initio* methods

- **DFT input**
- **Structure and Energetics** - Ti-bonding
- **Kinetics** - Rate-limiting steps in modeling H_2 desorption at surfaces for processes on time-scales of minutes



Electron Density Map on the [001] plane of Ti-Doped NaMgH3



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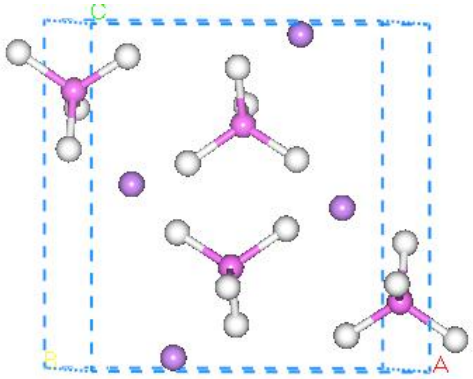
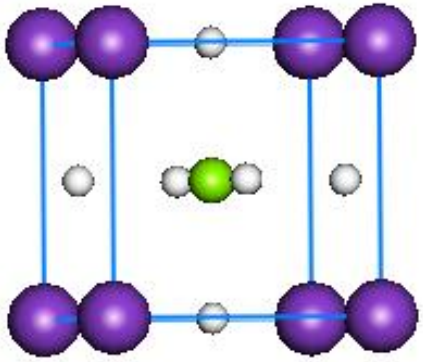
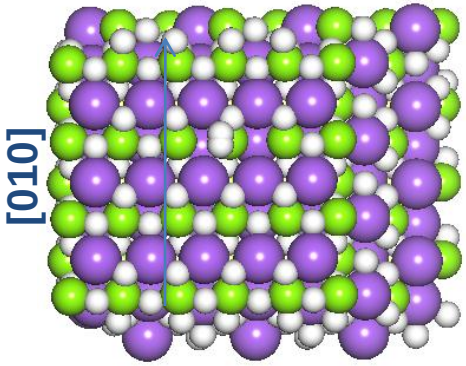
Focus 2

Kinetics of H Storage Materials

Models







Group Members

$LiAlH_4$

RET- Jeanine Edgecombe

Ph.D. Student- Purnima Karidehal

Free-Energy Barrier for H_2

↓

(73 KJ/mol H_2)

$KMgH_3$

REU- Mathew Wespetal

Undergraduate Student- Ashley Matthews

(102 KJ/mol H_2)

$NaMgH_3$

Ph..D. Student- Fernando Soto

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(68 KJ/mol H_2)

Numerical model for H dynamics and thermodynamics

- Mathematical model: H_2 absorption/desorption in a 3D metal-hydrogen cylindrical reactor using a finite difference/control volume scheme to solve it.
- Target: 3D $LaNi_5 – H_2$ in a cylindrical reactor, for comparison with the experimentals of Butler/LSU.
- Goal: inverse algorithm to determine the critical parameters for thermodynamics and rates of hydrogen absorption/desorption.

Focus 2

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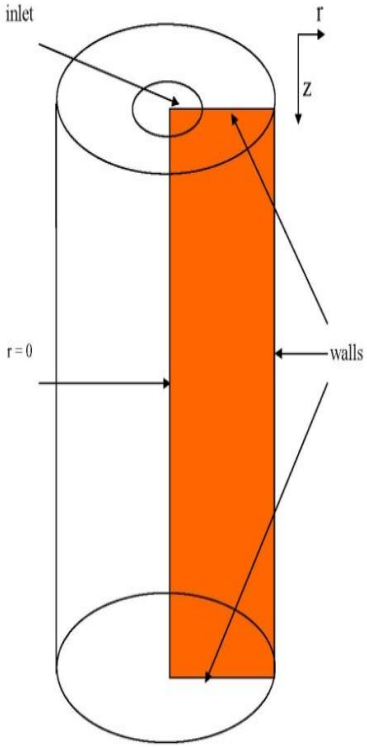
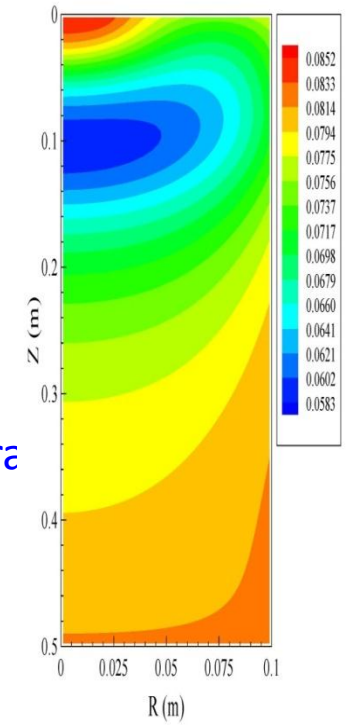
Modeling H adsorption/desorption in a cylindrical reactor

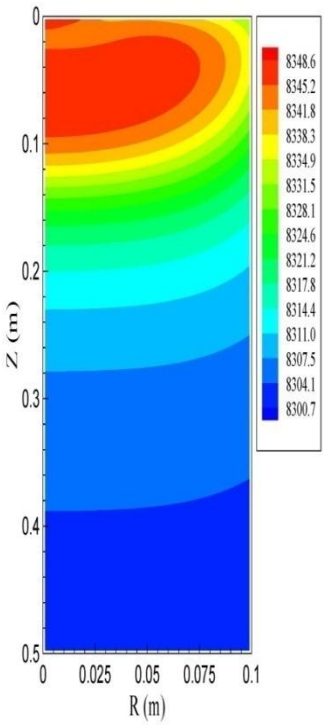
Evolution of H_2 desorption after 30 minutes.



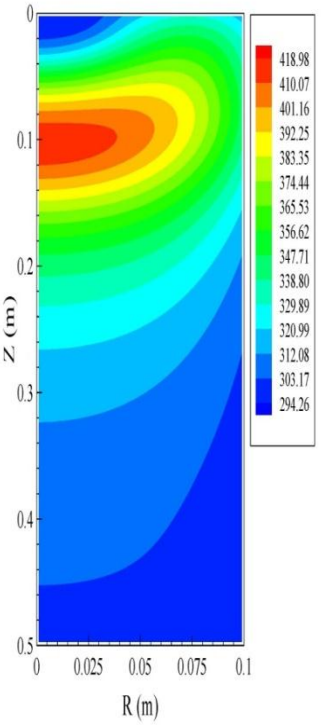
$LaNi_5$-H_2



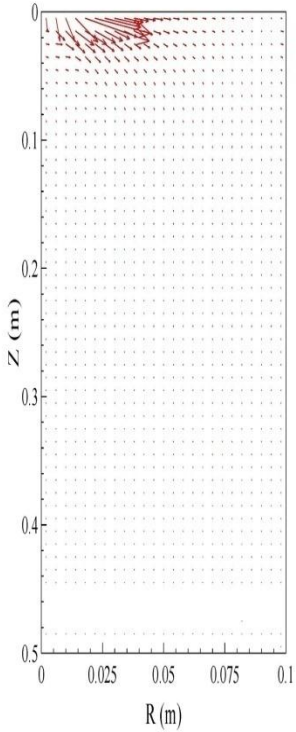
H_2 density



$LaNi_5$ density



Temperature



H_2 velocity

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Focus 2

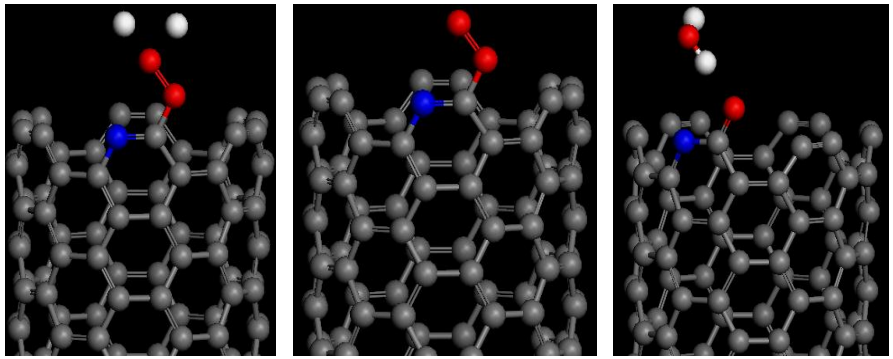
New catalysts for H_2 fuel cells

- Platinum-on-carbon electrodes are essential to conventional fuel cell designs. But platinum is rare and expensive.

- Nitrogen-doped carbon nanotubes (N-CNTs) show promise as alternative fuel cell catalysts [Dai *et al*., *Science* ***323***, 760 (2009)].

- G.-L. Zhao and F. Gao/SUBR carry out DFT calculations using VASP and GGA electron density functionals.

  O_2 can be absorbed and reduced on N-CNT edges.



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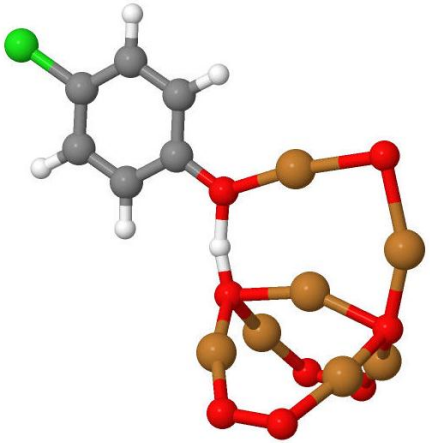
Focus 3

Catalytic processes for fuel generation and bi-product minimization

- Copper and iron oxide nanoparticles catalyze the formation of potentially carcinogenic free radicals.
- *Ab-initio* calculations on small clusters compare with experiment on larger clusters and model nanoparticle surfaces.
- Alumina is a common catalyst support.
- *Ab initio* studies have investigated the behavior of alumina-supported catalysts, but we need to simulate larger systems.
- ***We are developing force fields to be able to carry out larger scale simulations*.**



Focus 3

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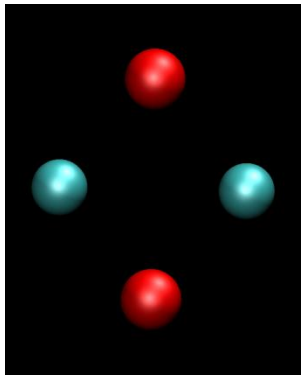
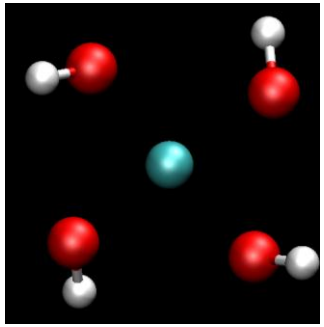
Force field parameterization: clusters that model crystal interactions

- DFT calculations
- Model: charge-dependent environment
- Success with Al_2O_3, FeO, and FeO_2



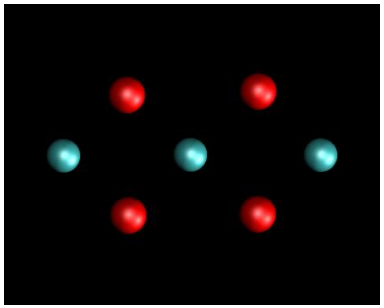


CuO crystal Structure

Property	Experiment	Predicted
α	90°	90.3°
β	99.6	96.9°
γ	90°	91.0°
a (Å)	4.68	4.56
b (Å)	3.42	3.55
c (Å)	5.13	5.03

Comparison of atomization energies (into neutral atoms)

	DFT	model
Cu_3O_4	-334.8	-331.8
Cu_2O_2*	-185.5	-185.4
Cu_3O_3	-338.0	-333.4
Cu_4O_4	-475.6	-439



*Only system we parameterized except $Cu(OH)_4$

Focus 3 → **SD1**

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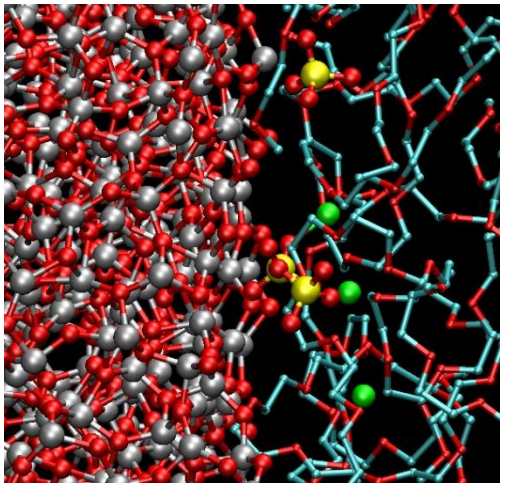
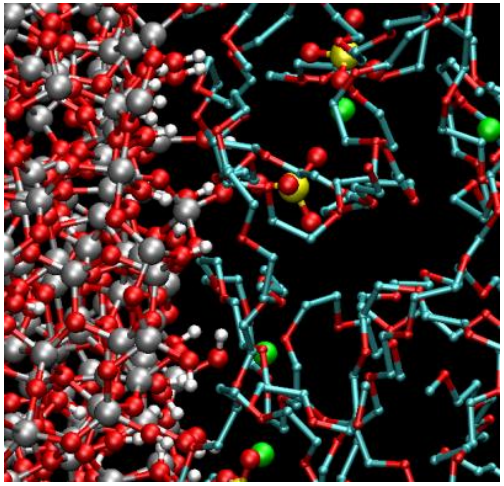
Improvement of lithium ion transport in polymer electrolytes

$D^{xyz}_{Li} \times 10^{-8}$	BULK	0.31 ± 0.02
$D^{xy}_{Li} \times 10^{-8}$	**ACID**	**0.75 ± 0.16**
(cm^2/s)	BASE	0.45 ± 0.06
D^{xyz}_{ClO4} x10^{-8}	BULK	0.78 ± 0.07
D^{xy}_{ClO4} x10^{-8}	ACID	1.32 ± 0.28
(cm^2/s)	BASE	0.71 ± 0.09

Basic



Acidic



- Polymer electrolytes are safer and more durable than traditional liquid electrolytes, but they slow lithium ion transport. Polymer blending might help.

- In agreement with experiment, simulation lithium ion mobility is enhanced near (within 30 Å) an acidic alumina surface.

Croce, F.; *et al.*, *Electrochim. Acta* **2001**, *46*, 2457.

New Focus

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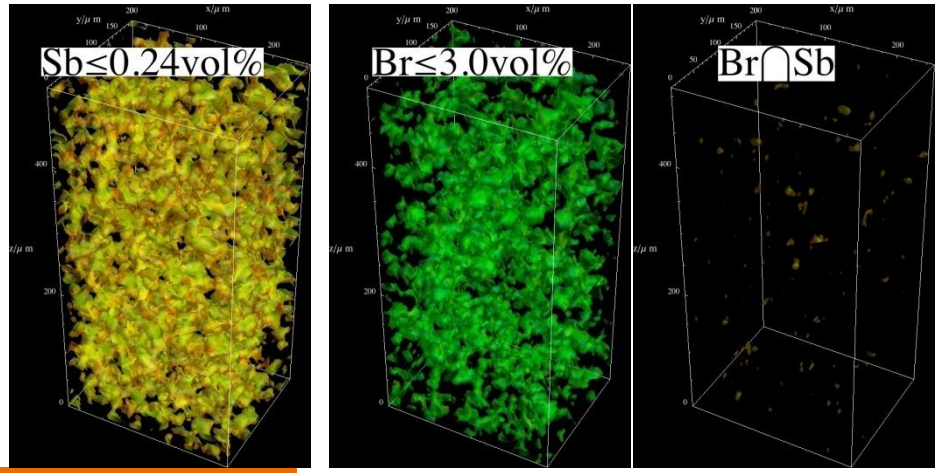
Tomography for real-time 3d imaging

- Help development of $20M SNS VENUS tomography beamlineL
- Large datasets and algorithms
- Image with polychromatic neutron beam with dynamic tomography data acquisition. Fire retardants, one with Sb, and the other with Br
- There is a lot space without one or the other, but almost all volume has some Sb or Br present.



Sb and Br retardants work cooperatively to maximize the volume occupied by retardant.

New Focus

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