LA-SiGMA

Louisiana Alliance for Simulation-Guided Materials Applications

Materials for Energy Storage and Generation

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Louisiana Tech University and Tulane University

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Focus Areas

1) *Electrical double-layer supercapacitors*, liquid electrolyte filling a carbon nanotube (CNT) forest

2) Optimizing *hydrogen storage* material properties combining modeling from atomic to macro-scale

3) *Catalysis* and development of new force fields for molecular modeling

4) *New focus:* understanding polymer blends and how *lithium ion batteries* work

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Molecular mechanisms for electrochemical double layer supercapacitors based on CNT forests

- *Battery:* slow charge/discharge, and degrades with each cycle
- *Supercapacitor:* rapid charge/discharge, holds less energy, but can charge/recharge many more cycles than batteries
- Combinations will be used in most practical systems.
- Understanding molecular mechanism will help in optimizing efficiencies and lifetimes.
- N. Pesika, L. Pratt, (Tulane), and S. Rick (UNO) collaborate, using a combination of *ab initio* methods, large scale molecular simulations, and experiments.

Focus 1

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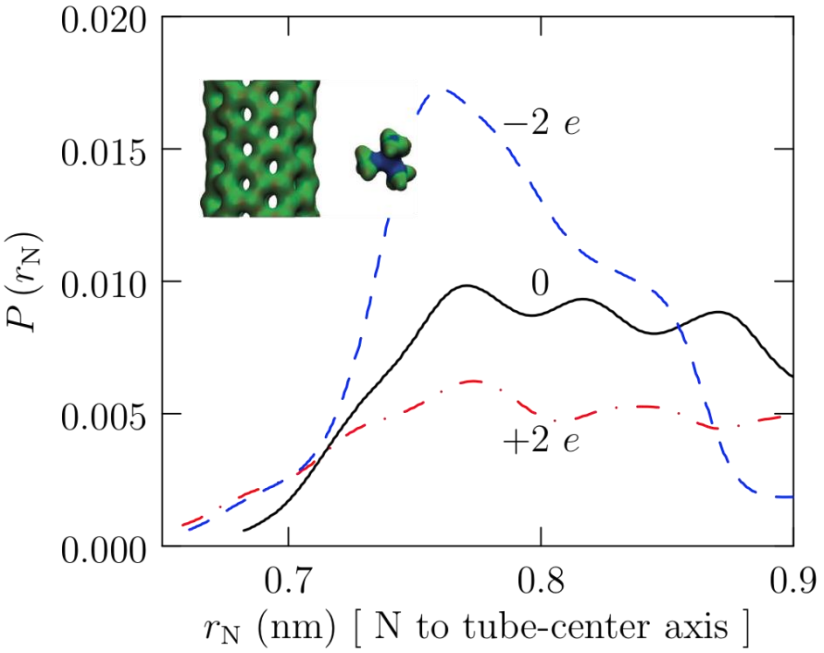
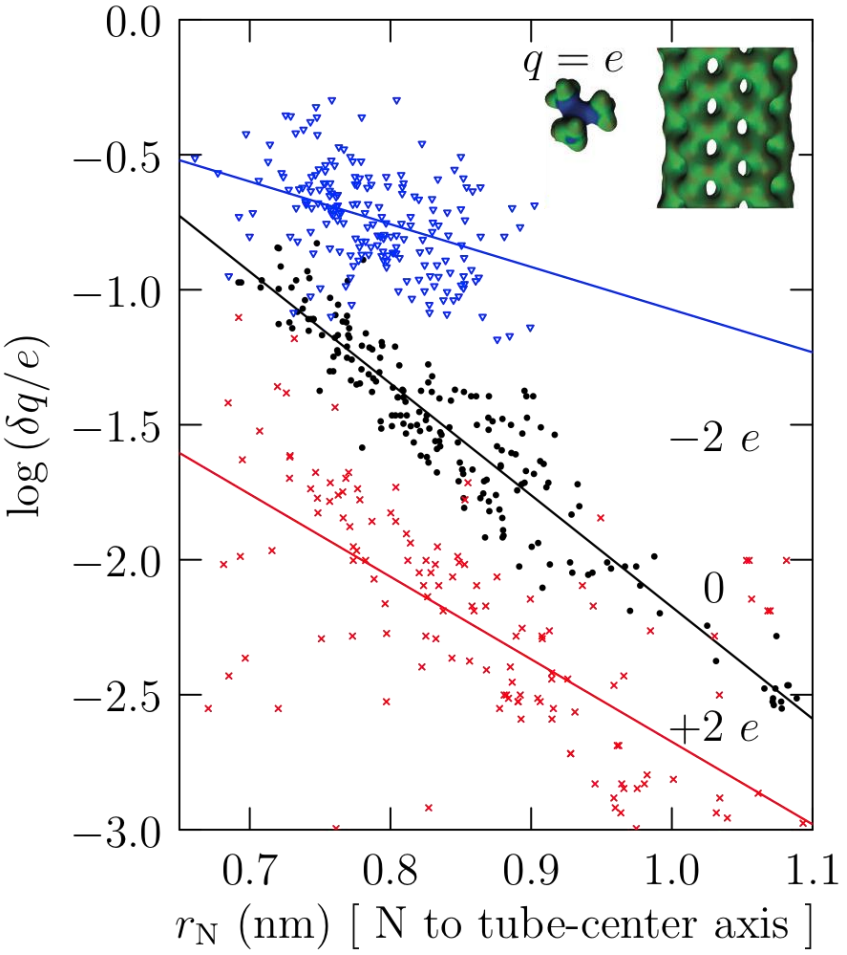
Charge transfer from a CNT electrode to a $(CH_3)_4N^+$ ion by *ab initio* molecular dynamics

- W. Zhang, G. G. Hoffman, S. W. Rick, and L. R. Pratt





Focus 1

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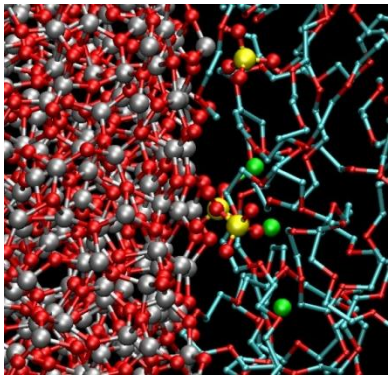
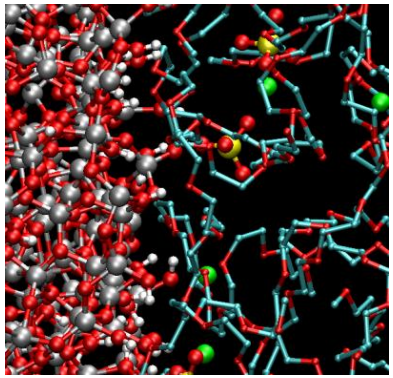
Transport in polymer electrolytes to improve lithium ion batteries

$D^{xyz}_{Li} \times 10^{-8}$	BULK	0.31 ± 0.02
$\boldsymbol{D^{xy}_{Li} \times 10^{-8}}$	**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: safer and more durable than traditional liquid electrolytes, but slow lithium ion transport.
- We find: *lithium mobility can be 2x enhanced next to acidic alumina* surface, in agreement with experiment.
- Enhancement not limited to the surface but extends into the melt.

New Focus

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

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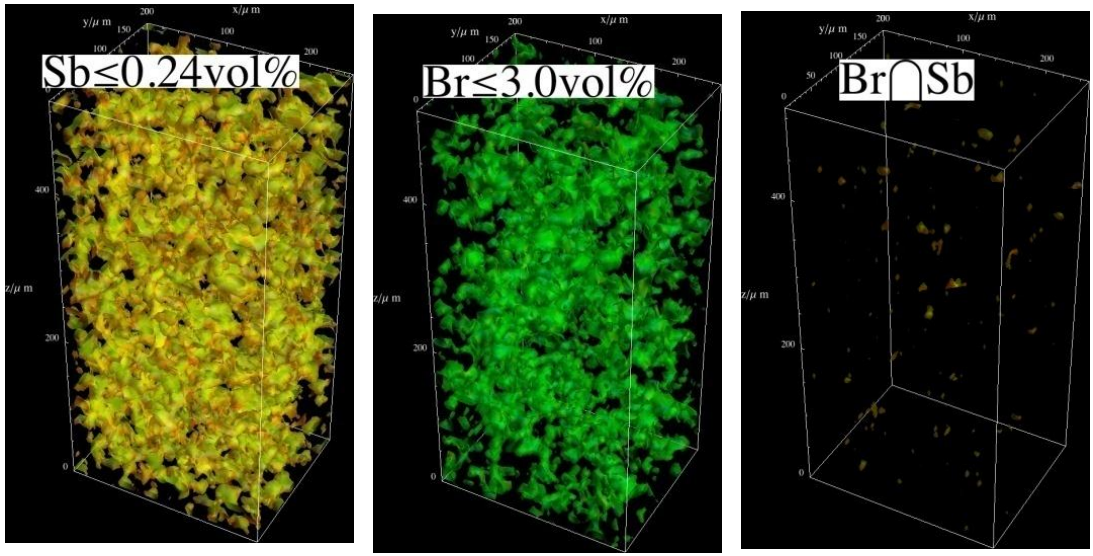
Tomography for real-time 3d imaging

- Develop the science case for $20M SNS VENUS tomography beamline
- Large datasets and complex algorithms to make sense of them

- Current technology cannot examine new Al plus B flame retardants.
- *New:* phase-contrast X-ray imaging, which should be able to image these.
- This technology will also *image lithium ion battery cathode wear*.

Black: flame retardant present



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

New Focus

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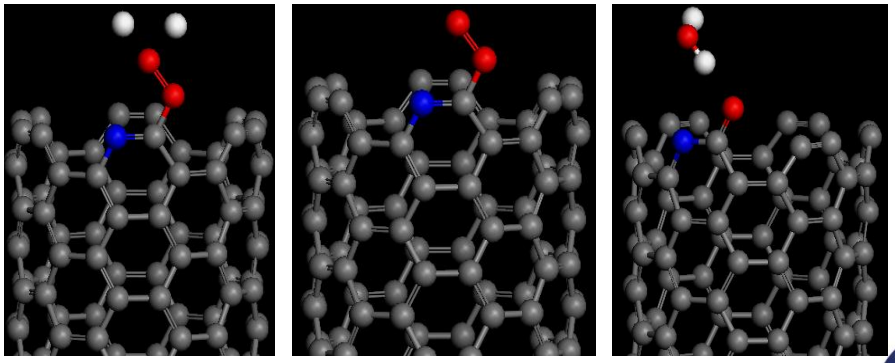
Catalysts for hydrogen fuel cells

- Pt as a fuel-cell catalyst is rare and expensive.
- Promising alternative to Pt: *nitrogen doped carbon nanotubes* (N-CNTs) [Dai *et al*., *Science* ***323***, 760 (2009)]
- DFT calculations (*VASP and GGA functionals*): O_2 can be absorbed and reduced on the N-C complex site (Pauling site) at the edge of N-CNTs.

Guang-Lin Zhao and **Feng Gao (**SUBR) identify reaction sites for hydrogen fuel cell catalysts.



Focus 1

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Critical issues for hydrogen storage

- Hydrogen storage *capacity* by weight and by volume
- Reliable *fast kinetics* for hydrogen absorption/desorption
- *Ab initio electron density functional* methods are good at essential atomic-scale energetics, but have difficulty with dynamic and multi-scale properties.
- We are developing a multi-scale approach combining the expertise of several specialists to link the atomic level with large scale and dynamic properties.

Multiple disciplines and institutions to investigate hydrogen storage

Researcher	Institution	Area of Expertise
Daniela Mainardi	LA Tech	Periodic ab initio calculations and dynamics
Les Butler	LSU	Imaging materials in real time
Randy Hall	LSU (just left)	Ab initio calculations
Bin Chen	LSU	Force field development and molecular simulation
Weizhong Dai	LA Tech	Macro-scale simulation

Focus 2

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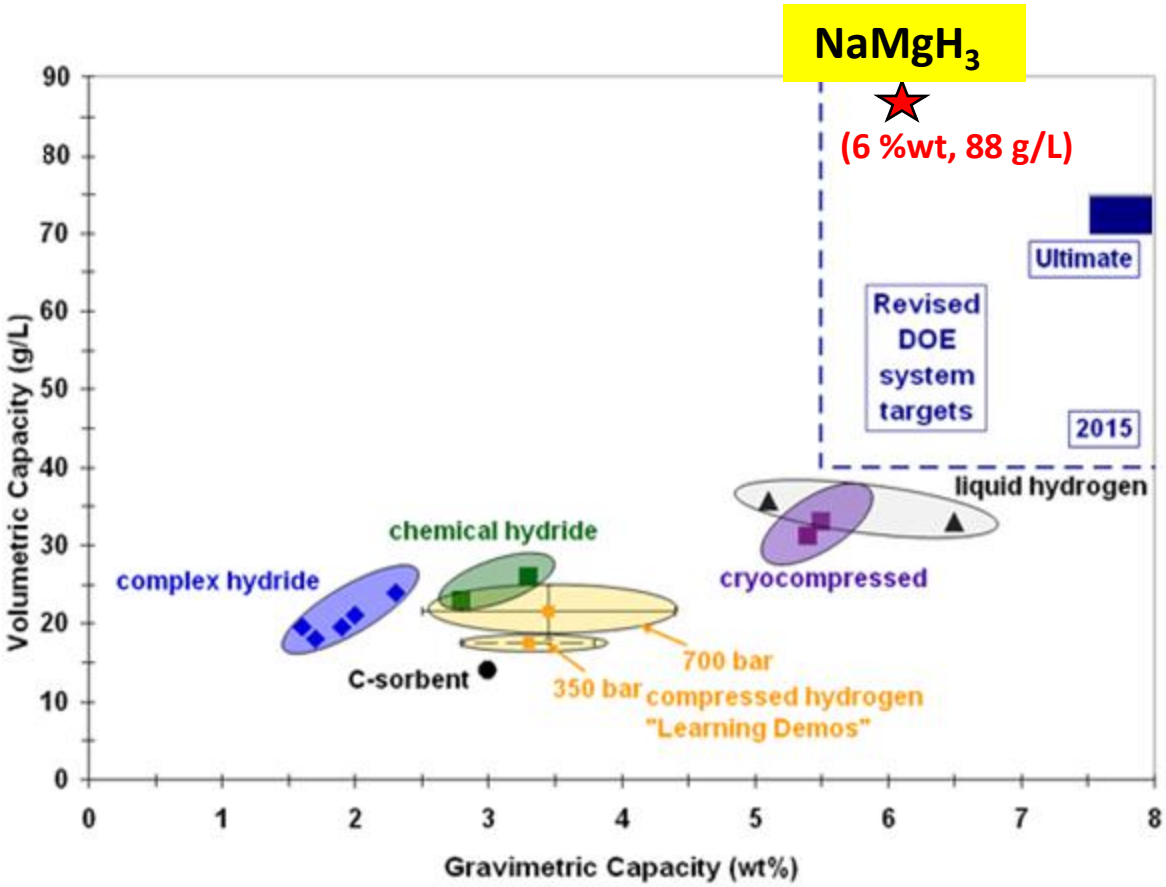
DoE Technical Targets for 2015: 5.5 % wt.

Consumers want a vehicle that refills rapidly

- Necessary charge and discharge of hydrogen fast

- Reduce cost of fuel cells while improving durability
- Storage capacity must be big enough to attain viability



"Status of Hydrogen Storage Technologies". Energy.gov. U.S. Department of Energy. March 12. 2012..

Focus 2

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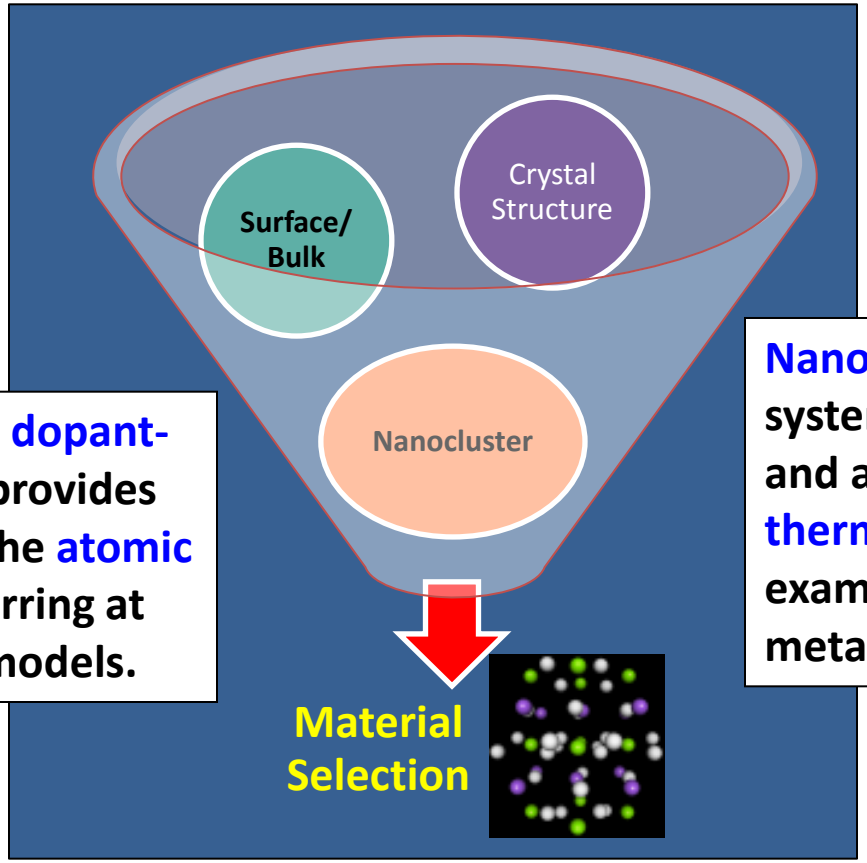
Approach for improving hydrogen storage based on *ab initio* methods

Accurate determination of crystal structures and their energetics provide detailed knowledge about the dopant preferred site that facilitates hydrogen re/dehydrogenation.

Plane-Wave Density Functional Theory (DFT)



DFT Coupled Molecular Dynamics (DFT-MD)

Investigations of the dopant-hydride interaction provides unique insight into the atomic scale processes occurring at the surface or bulk models.

Nanoscale hydrogen storage systems may offer faster response and advantageous thermodynamics compared to, for example, bulk or micrometer-sized metal hydrides

Focus 2

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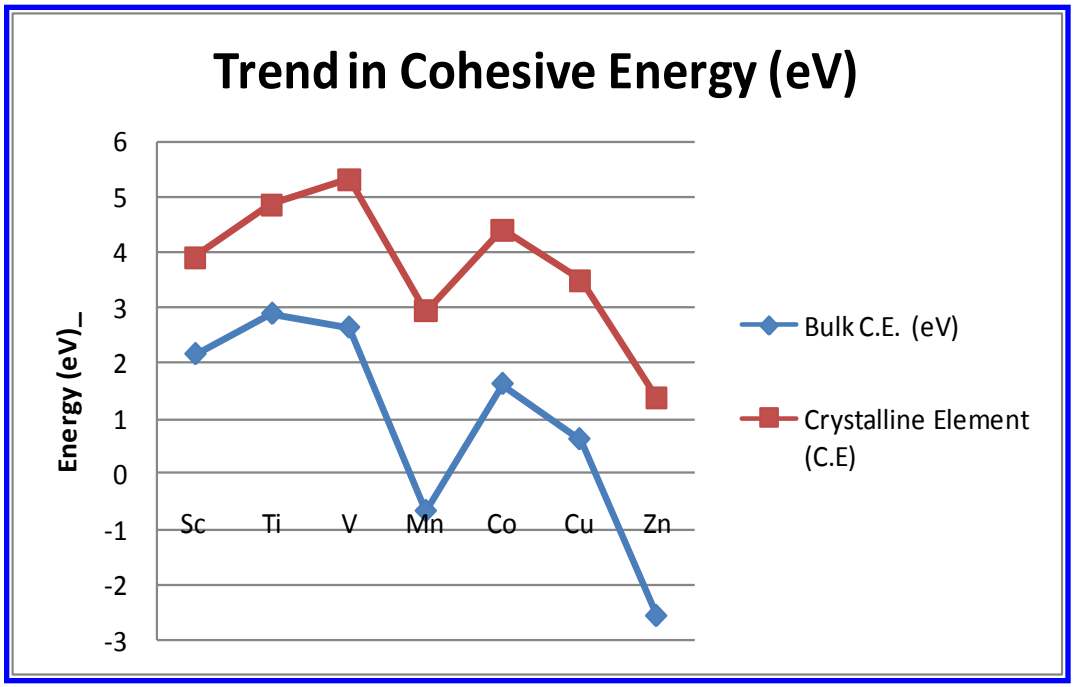
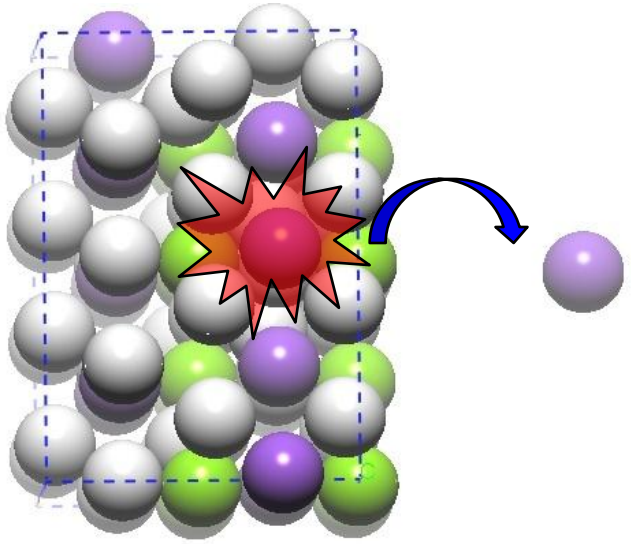
Cohesive Energy for 3*d* Transition Metals





- Cohesive Energy is calculated relative to the pure model
- The higher the cohesive energy in crystalline element, the higher the energy in bulk model.

$$E_{cohesive} = E_{total\ system} - \sum E_{free\ neutral\ atoms}$$

Relative C.E. (eV) = Doped Model C.E.- Pure Bulk C. E.

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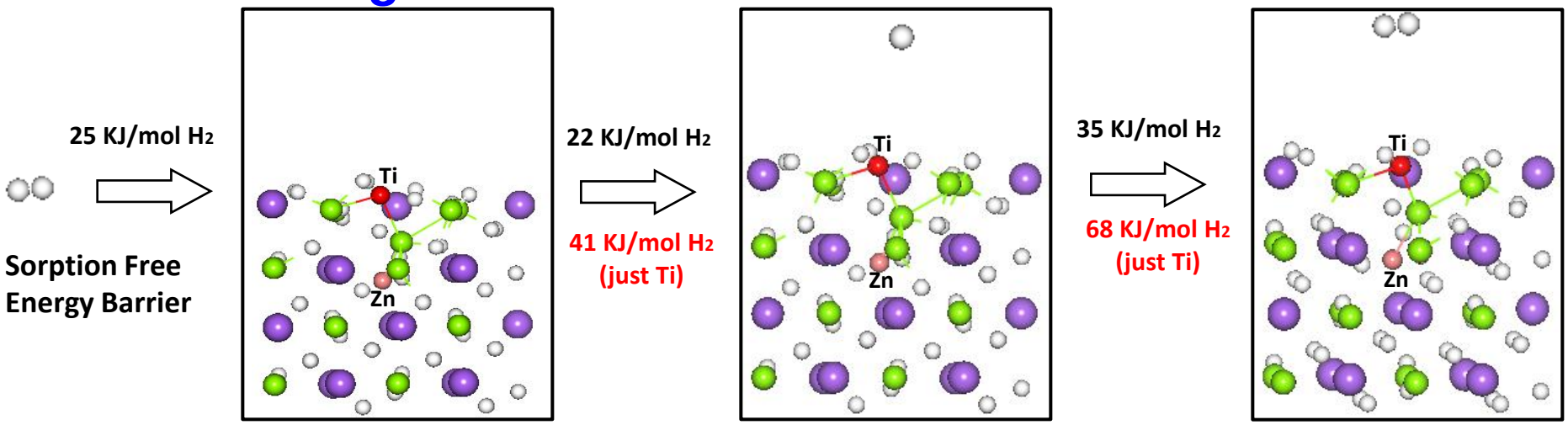
Ab initio calculations and the role of dopants on hydrogen storage materials

Ti is placed at the surface and Zn at a bulk site in the subsurface region:



- **Ti attracts extra hydrogen** atoms by positioning itself in the **subsurface area**; **creating disorder** in the crystal
- **Zn-H and Mg-H** nearest neighbor distances **increase** when hydrogen atoms are removed

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Macro-scale model for thermodynamics & kinetics of hydrogen absorption / desorption

- Analyzes the hydrogen absorption/desorption in a 3D cylindrical reaction volume using a finite difference/control volume scheme.
- *Currently:* $LaNi_5 - H_2$ in 3D a cylindrical reactor
- *Future:* compare with the experimental results of Butler (LSU)
- *Goal:* inverse algorithm based on the simulation and experiment to determine the important parameters for hydrogen absorption/desorption processes

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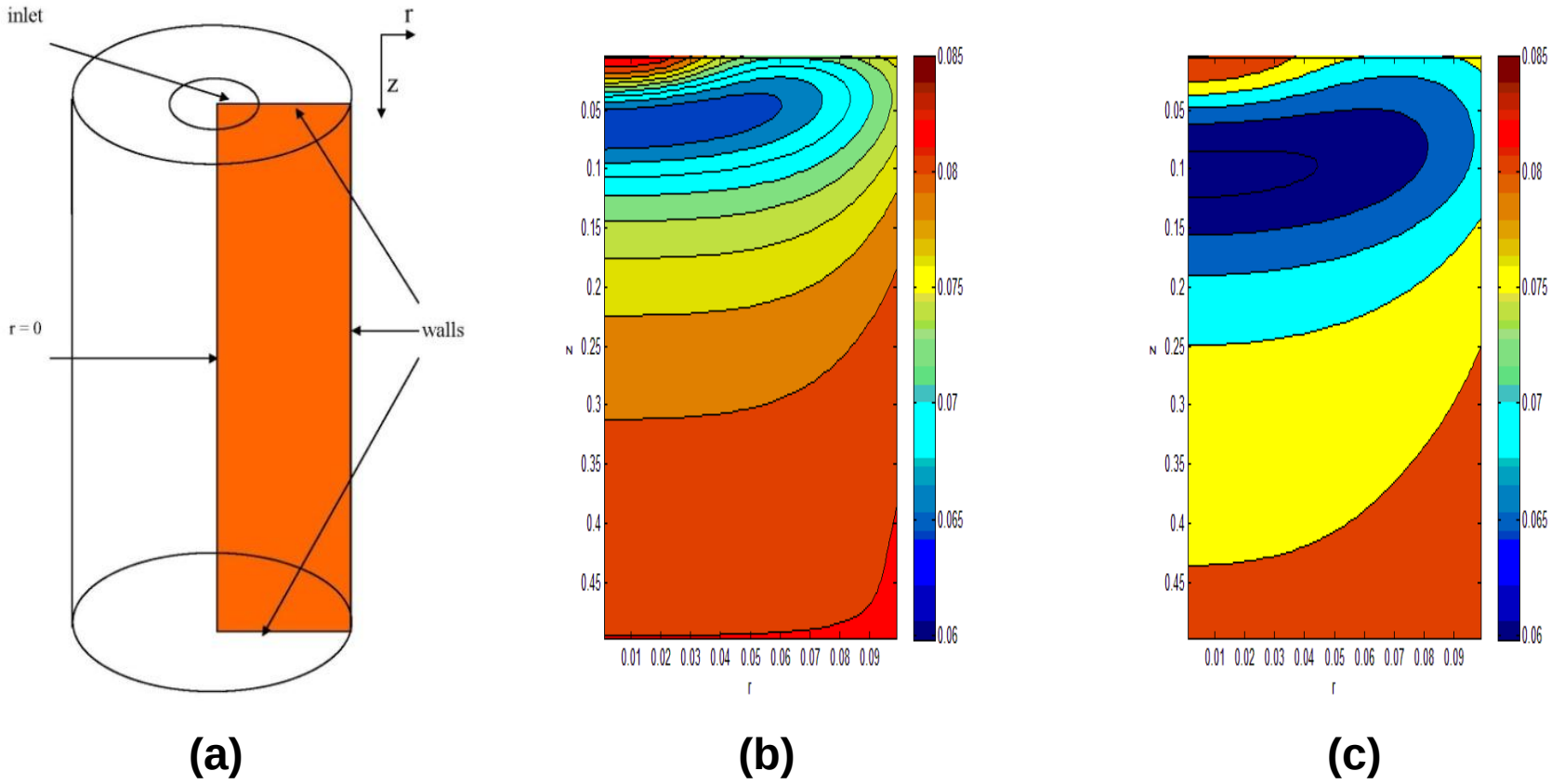
Hydrogen adsorption in a cylindrical reactor



(a) **(b)** **(c)**

Fig. 1. (a) Reactor and cross section, and contours of hydride density distribution at times **(b)** t = 30 min and **(c)** t = 60 min.

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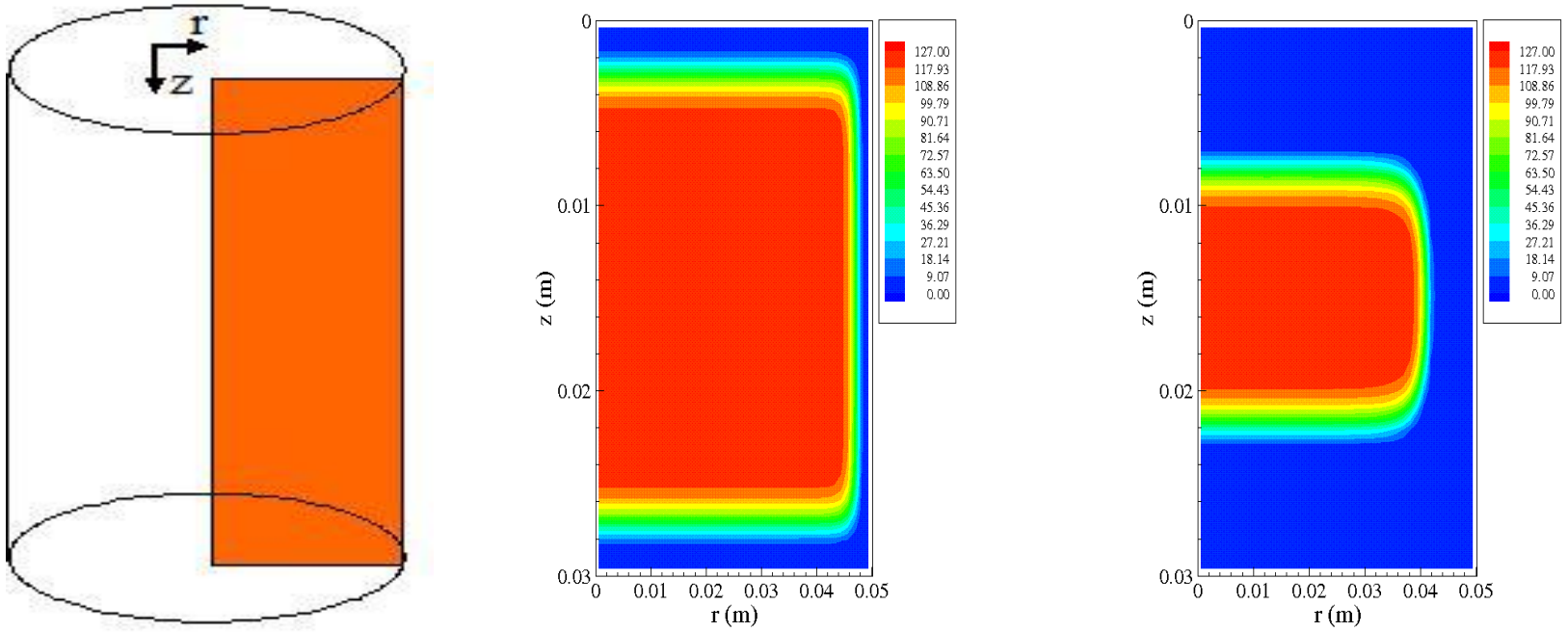
Hydrogen desorption in a cylindrical reactor



(a) **(b)** **(c)**

Fig. 2. (a) Reactor and cross section, and contours of hydride density distribution at times **(b)** t= 10 min and **(c)** t = 30 min.

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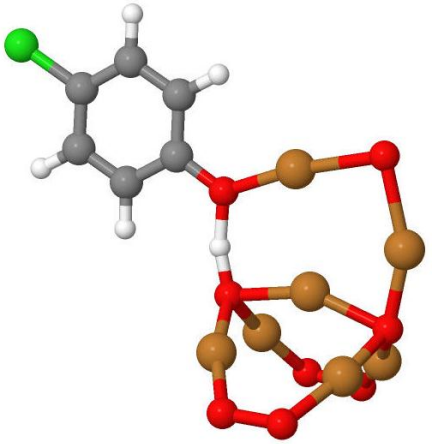
Catalytic processes for fuel generation and modeling combustion biproducts

- *Copper and iron oxide nanoparticles* catalyze the formation of carcinogenic free radicals, dioxins and furans from combustion organics.
- *Ab initio* calculations of small clusters to compare with experiment
- Alumina is a common support for catalysis
- Many *ab initio* studies have investigated alumina supported catalysts, but we need to simulate larger systems.
- **We are developing force fields to be able to carry out larger scale simulations.**



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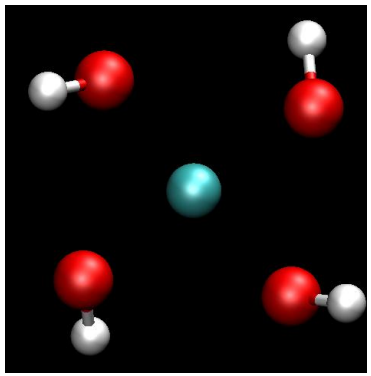
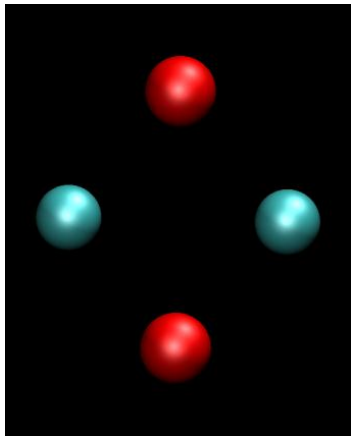
Force fields: from clusters to the crystals

- *DFT calculations:* MO6 functional and aug-cc-pvdz basis set and CHELP-G charges of small clusters below
- *Model:* charge depends on environment, *e.g.,* number and type of bonds
- Oxygens surrounding copper resulted in a higher charge.
- *Success:* 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





Focus 3 → **SD1**

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SD2 Focus 1 Milestones

Milestones	Y1	Y2	Y3	Y4	Y5	
Simulation of pore filling in CNT forest capacitors .	X	X				On Track
Study chemical damage at elevated electric potentials.	X	X	X			On Track
Optimize computational efficiency of ab initio MD techniques.	X	X				Complete
Study role of quantum capacitance in electrochemical capacitance.		X	X	X		Ahead
Explore additional nanoforest-based capacitor systems.			X	X	X	
Predict catalytic sites in nanotubes.		X	X	X	X	On Track
Design, build, and test fuel cells and use results to guide new calculations.			X	X	X	

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SD2 New Focus Milestones

Milestones	Y1	Y2	Y3	Y4	Y5	
Study the effects of solid surfaces on lithium ion mobility.	X	X				*On Track*
Image lithium ion cathode wear in real time.		X	X			*On Track*

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SD2 Focus 2 Milestones

Milestones	Y1	Y2	Y3	Y4	Y5	
Extend MC methods to calculate free energies of H_2 uptake in storage materials.	X	X	X	X	X	*On Track with modifications*[1]
Use existing force fields to calculate H_2 uptake in bulk alloys.	X	X	X	X	X	*On Track with modifications*[2]
Develop finite element model to track 3D microstructure evolution.		X	X	X		*On Track*
Perform X-ray nanotomography imaging of H_2 uptake. [Argonne's Advanced Photon Source (APS), and neutron tomography at NIST]	X	X	X	X	X	*On Track, but emphasis changing*[3]

1) Using grand canonical ensemble methods coupled to a novel insertion/removal strategy.
2) Team developed own force field to study of $KMgH_3$. Additional force fields are in development. Also have decided to use finite element modeling coupled to Kinetic Monte-Carlo (KMC) simulations to understand H_2 uptake by various alloys on multiple length and time scales
3) Shifting away from H_2 storage to tomography studies of chemical changes in the electrodes of lithium ion batteries during charge and discharge cycles.

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SD2 Focus 3 Milestones

Milestones	Y1	Y2	Y3	Y4	Y5	
Develop force fields for one metal oxide system.	X					*On Track*
Study water gas shift and Fischer-Tropsch reactions.	X	X	X			*On Track*
Study persistent free radicals production on metal oxide clusters.	X	X				*On Track*
Develop new force fields and study of additional catalytic processes.		X	X	X		*On Track*
Validate force field calculations with experimental measurements and DFT calculations.			X	X	X	*On Track*

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