LA-SiGMA

Louisiana Alliance for Simulation-Guided Materials Applications

Materials for Energy Storage and Generation

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We are investigating materials for energy storage and generation

- Focus 1: Molecular level mechanism for electrical double-layer supercapacitors via a liquid electrolyte in a nanotube forest
  - Calculating band gap properties of semiconductors
- Focus 2: Mechanism for hydrogen storage, and developing a procedure to optimize hydrogen storage material properties via a multi-scale approach
- Focus 3: Developing force fields for the simulation of catalysis
- New Focus: understanding how lithium ion batteries work

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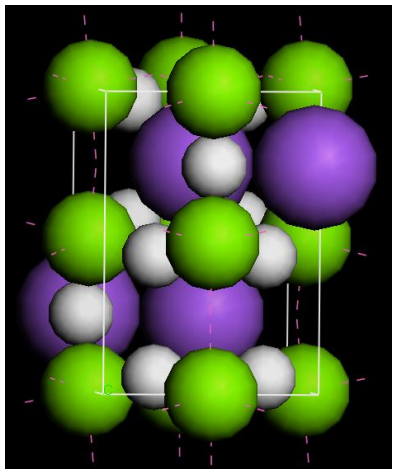
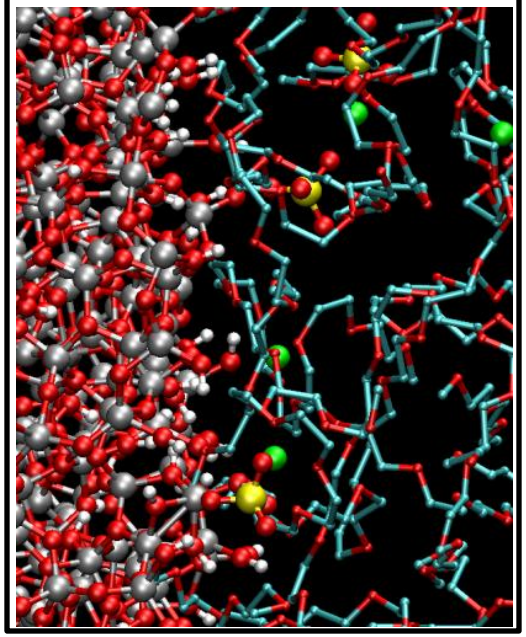
We are developing a multiscale approach to investigate

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 electron structure to guide the parameterization of atom based molecular model

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Goals and Milestones

- Recruit, engage, and mentor a gender and ethnically diverse group of students and postdocs. Our progress is described in "Diversity, Workforce Development, and External Engagement" (at 2:00-2:30 p.m.).

- Conduct simulation of pore filling in electrochemical capacitors based on nanowire forests, and understand the role of quantum capacitance. Our progress is described in focus 1.

- Develop algorithms that combine chemistry and physics of energy storage. Our progress is described in focus 2.

- Develop new force fields for catalytic processes based on DFT functionals. Our progress is described in section 3.

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The molecular level mechanism for electrochemical double layer supercapacitors is being investigated

- Supercapacitors are used for energy storage when many cycles and a high power density are required, and their degradation is slow and they can be charged/discharged rapidly
- How the mechanism for capacitance work on the molecular level will aide in enhancing their efficiency and lifetimes.
- A group including L. Pratt, N. Pesika, at Tulane, along with S. Rick at UNO are investigating this using a combination of *ab initio* methods, large scale molecular simulations, and experiments.

Focus 1

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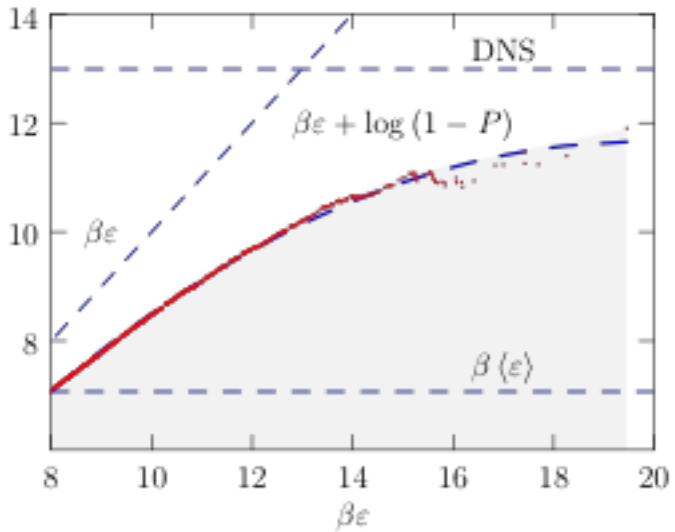
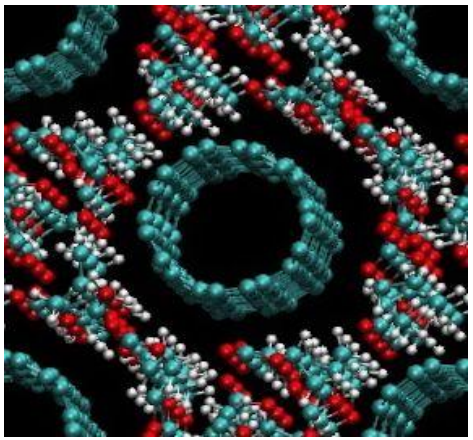
We found that the filling of nanotube forests is unfavorable

- We used density functional theory (DFT) based molecular dynamics (MD) for our calculations
- Under certain conditions, the filling of nanotube forests can increase the free energy of the system, making it thermodynamically unfavorable
- This is in contrast to experimental results, and may be due to a lack of dispersion interactions in the theory used.





Focus 1

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We need to improve the density functional methodology

- The DFT used does not take into account dispersion interactions between molecules
- We are currently building dispersive interactions into the DFT methodology to see if it improves agreement with experiment.
- We plan to keep using DFT-MD to investigate these systems, due to their ability to pick up “quantum capacitance” in addition to “double layer” capacitance.
- We are also developing a new molecular model to facilitate the ability to carry out larger scale simulations of these systems.

New semiconductor materials is important for the development of electronic materials

- The band gap of an electronic material is imperative for its ability to work as a sensor or to emit light of a certain frequency
- We are developing methods to accurately calculate the band gap of a material computationally
  - G.L. Zhao and D. Bagayoko, Southern University, Baton Rouge
- We have done this successfully for ZnO, CdS, TiO_2 and more semiconducting materials with high accuracy.
- This will be used to guide the design and fabrication of new semiconductor materials.

Focus 1

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We will work to address the critical issues of hydrogen storage

- Hydrogen storage becoming viable depends on materials holding enough hydrogen by weight and volume, having the proper thermodynamic properties (so hydrogen releases at a certain temperature), and fast kinetics for hydrogen absorption/desorption.
- Ab initio methods are good at providing a qualitative understanding of the behavior of hydrogen in storage materials, but have difficulty making direct comparisons with experiment for dynamic and thermodynamic properties
- We need to build a multiscale approach using a variety of expertise to link the molecular level with large scale thermodynamic and dynamic properties

Focus 2

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A collaboration has been initiated spanning 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	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

Focus 2

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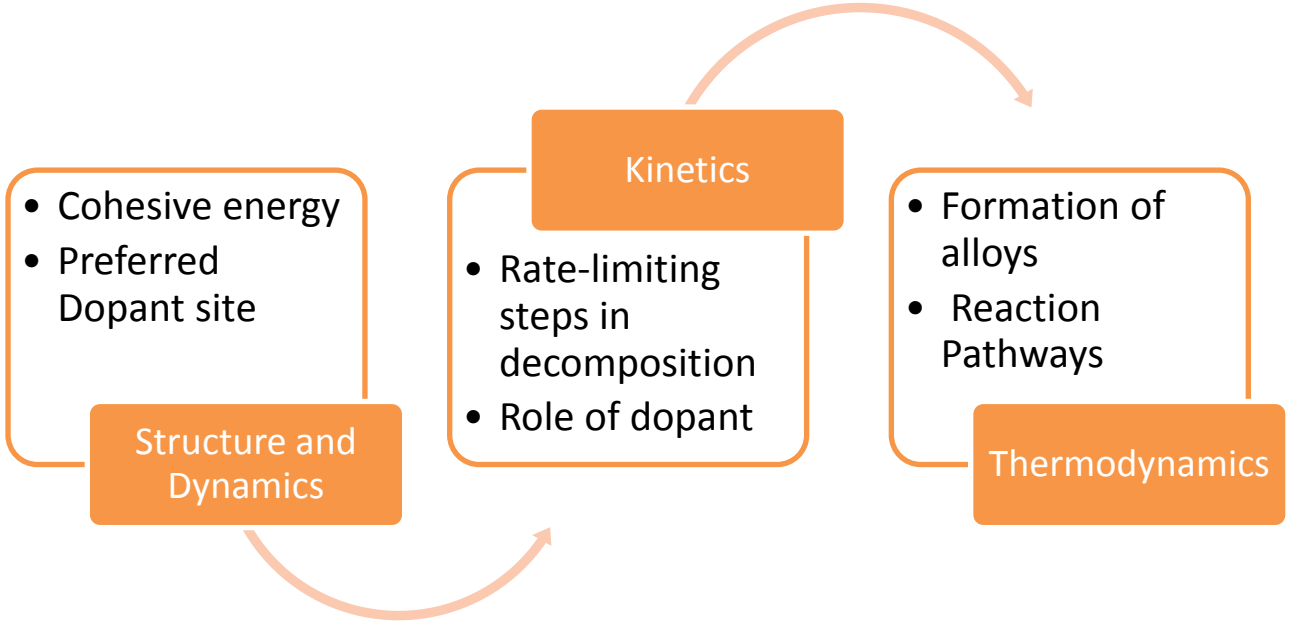
We have developed a strategy for improving hydrogen storage based on *ab initio* methods

- **Understanding and optimization of the thermodynamics and kinetics in hydrogen storage systems**
- **Goal** : Improve ability to design materials for hydrogen storage/explore wide range of promising hydrogen storage systems
- **Method** : First-principles investigation of effect of catalytic additives or **dopants** in improving atomic mobility and desorption rates in CMHs



Focus 2

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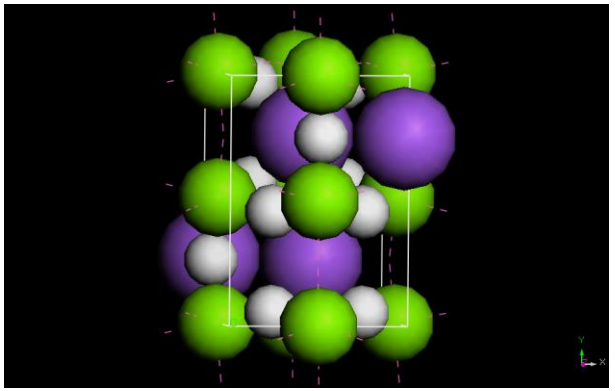
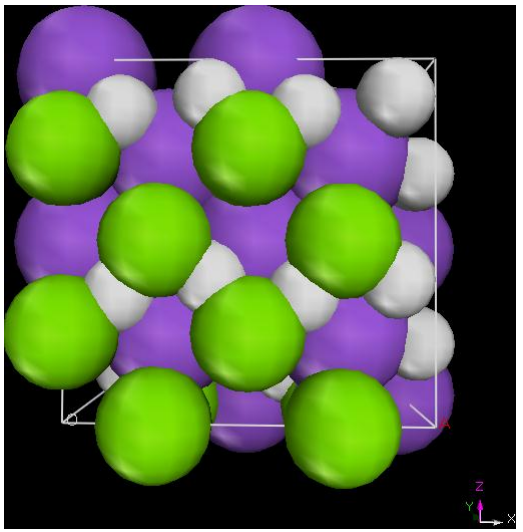
We are searching for additives to improve $NaMgH_3$

- **Complex Metal Hydrides** have attracted interest, experimental findings show that decomposition temperature for these can be modified by introduction of additives



- **Structure and Dynamics Stage**
  Overall goal of First Principles calculations for 3d-Transition Metal **Doping** is to determine**:**
  - Structural stability
  - Preferred doping site
  - Cohesive energy



Focus 2

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We have a better understanding of how dopants affect $NaMgH_3$ for hydrogen storage

- Titanium is found to be the best dopant over a wide range of transition metals surveyed (vandium also showed promise).

- Substitution of Ti with Na atom shows that the Ti nearly equally prefers to be at the hollow site and at the sodium lattice site, having equal energies.

- Putting Ti @ hollow site may cause the percolation of resulting sodium atoms through the bulk of the materials, creating Na rich and Mg rich sites, potentially creating more space for hydrogen sorption/desorption.

Focus 2

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Ways to link structural information with thermodynamic properties are being sought

- A force field is being developed to allow the simulation of much larger systems than can be done with ab initio methods.
- We will be able to make direct comparisons with experiment for the thermodynamics of hydrogen uptake via Monte Carlo simulations
- Currently, we have found good agreement with experiment for the energetics and structure of $LaNi_5$ and $LiNi_5H_6$ solids
- This is currently being extended to the systems being studied with ab initio methods.

Focus 2

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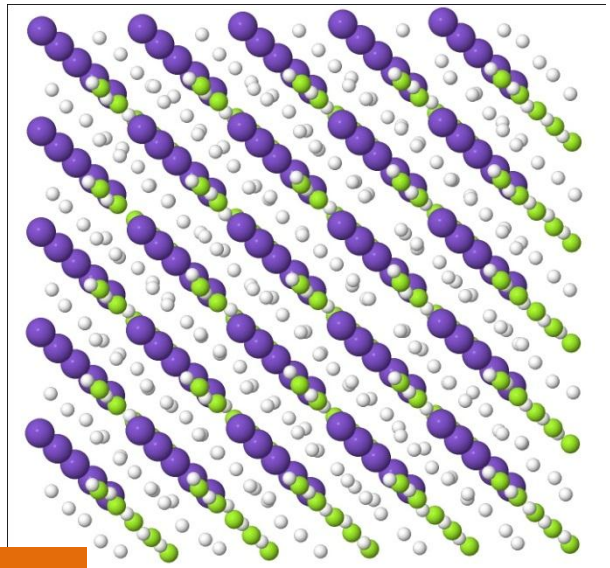
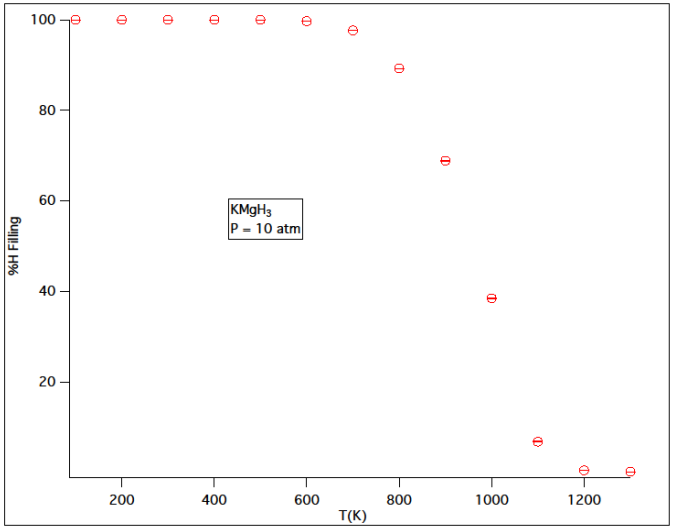
Preliminary work allows us to predict the transition points for hydrogen loading/unloading

- We are working to understand how the KMg structure changes with respect to hydrogen loading.
- With time, we can use this to predict how the addition of dopants influence the transition state points without the need to synthesize them, and also to understand it on the molecular level





Focus 2

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A numerical model to estimate hydrogen dynamics and thermodynamics is being developed

- Our mathematical model analyzes the hydrogen absorption /desorption in a 3D metal-hydrogen cylindrical reactor using a finite difference/control volume scheme to solve it.
- We are currently investigating a 3D $LaNi_5 – H_2$ in a cylindrical reactor, and in the future will compare with the experimental results of Dr. Butler at LSU
- In the future we will develop an inverse algorithm based on the simulation and experimental data in order to determine the important parameters to improve the rate of hydrogen absorbed /desorbed, and thermodynamics and thermo-physical properties

Focus 2

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We are developing tomography strategies for real-time 3d imaging

- Help develop the science case for the estimated $20M SNS VENUS tomography beamline
- We collect very large datasets and need complex algorithms to make sense of them
- Image with polychromatic neutron beam (high flux) with novel dynamic tomography data acquisition (Golden ratio).

- We are finding that in successive hydrogen absorption runs, certain metal sites are more active than others for hydrogen absorption.
- We need better particle tracking algorithms to confirm this.
- If confirmed, what characteristics of these sites improve hydrogen absorption?

The movie shows slices along a metal cylinder of $LiNi_5H_6$,

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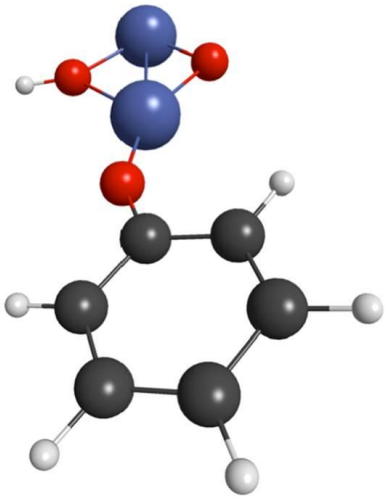
Catalytic processes are important for fuel generation and understanding biproducts from combustion

- Copper and iron oxide nanoparticles catalyze the formation of potentially carcinogenic free radicals, dioxins and furans from organics present in combustion.
- We have carried out *ab initio* calculations of small clusters of these to compare with experiment
- Need to simulate larger systems to model a nanoparticle surface
- Alumina is a common support for catalysis
- Many *ab initio* studies have investigated the behavior of alumina supported catalysts, but we need to simulate larger system
- **We will develop force fields to be able to carry out larger scale simulations**



Focus 3

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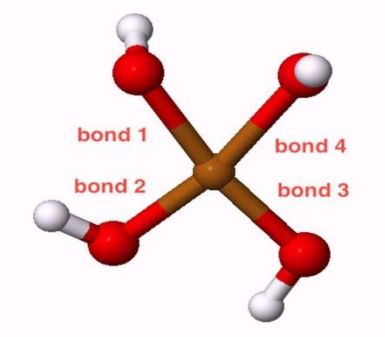
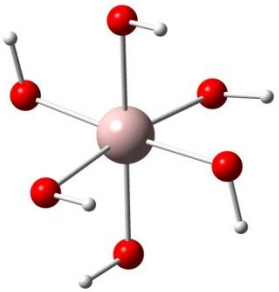
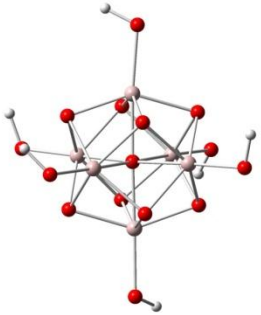
We are currently parameterizing a force field that will have a high degree of transferability

- R. Hall (LSU) is working with B. Ramuchandran and C. Wick (LA TECH) to develop new force fields to allow larger scale simulations of these systems
- We are employing a strategy of fitting to small *ab initio* clusters and refining our force field to agree with *ab initio* and experiment for larger periodic systems.
- Most currently available force fields appear to be based on pairwise interactions that will not be able to respond to the heterogeneous condition necessary for catalysis
- We have carried out *ab initio* calculations of copper oxide and alumina clusters, and are working on the initial parameterizing of our force field. Later, we should have a force field with a high degree of transferability.







Focus 3 → **SD1**

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We may expand this knowledge towards lithium ion batteries

- Lithium Ion batteries is expected to be a major area of future research growth.
- Imaging can serve a crucial role in optimizing the performance of lithium ion batteries
- Image LiC_6 electrodes to compute difference image to measure 3D electrochemical changes
  - This can be used to determine how lithium behaves during charging and recharging of worn batteries.
  - What specific factors determine battery wear and lifetime.

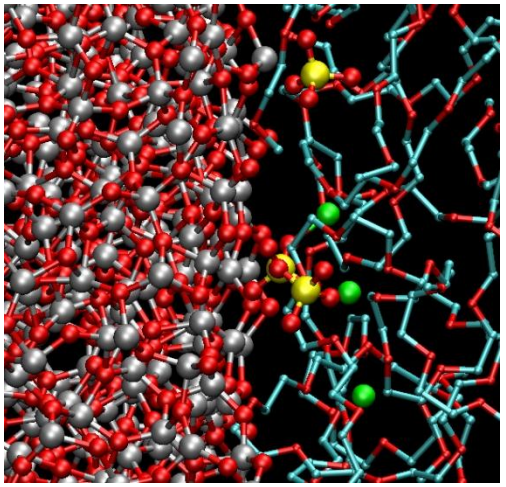
"Neutron Imaging of a Commercial Li-Ion Battery During Discharge: Application of Monochromatic Imaging and Polychromatic Dynamic Tomography", L. G. Butler, B. Schillinger, K. Ham, T. A. Dobbins, P. Liu, and J. J. Vajo, *Nuclear Instruments & Methods in Physics Research Section A-Beam Interactions with Materials and Atoms.,* in press (2011).

Spatio-temporal computed tomography of dynamic processes", A. Kaestner, B. Münch, P. Trtik, L. G. Butler, *IEEE Trans. on Geoscience and Remote Sensing*, (submitted).

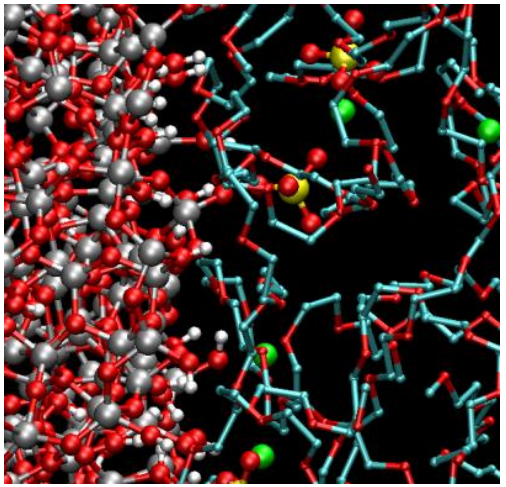
Understanding ways to improve lithium ion transport in polymer electrolytes

- Polymer electrolytes are much safer and durable than traditional liquid electrolytes, but have too slow of lithium ion transport for viable usage
- How is lithium ion transport influenced by its position with respect to an alumina surface?
- How do acidic groups versus basic groups change lithium ion transport near them?
- Experimental work found that spherical nanoparticles in poly(ethylene oxide) with acidic groups (hydrogen terminated) had faster lithium ion transport than those with non-hydrogen terminated or with no nanoparticles present.

Basic



Acidic



New Focus

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

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May I answer some questions?

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SD2 Focus 1 Milestones and score card

Milestones	Y1	Y2	Y3	Y4	Y5
Conduct simulation of pore filling in electrochemical capacitors based on nanowire forests.	X	X			
Incorporate chemical processes in electrochemical simulations to study chemical damage at elevated electric potentials.	X	X	X		
Optimize computational efficiency of *ab initio* MD techniques.	X	X			
Verify computationally the behavior of quantum capacitance in electrochemical capacitance.		X	X	X	
Explore additional nanoforest-based capacitor systems (Y 3-5)			X	X	X
Predict catalytic sites in nanotubes (Y 2-5)		X	X	X	X
Design, build, and test fuel cells and use results to guide new calculations (Y 3-5)			X	X	X

SD2 Focus 2 Milestones and score card

Milestones	Y1	Y2	Y3	Y4	Y5
Extend the AVUS-HR, Gibbs, expanded ensemble methods to hydrogen in solids and locate spinodal points; calculate free energies of H_2 uptake in LiH_x and other storage materials.	X	X	X	X	X
Use existing force fields to calculate H_2 uptake in bulk alloys; develop new force fields for new and existing alloys.	X	X	X	X	X
Develop finite element model to track 3D microstructure evolution and finite difference models for ionic diffusion rates using distances and times provided by experiments		X	X	X	
Perform X-ray nanotomography imaging of H_2 uptake in bulk alloys using Argonne's Advanced Photon Source (APS), and neutron tomography at NIST.	X	X	X	X	X

SD2 Focus 3 Milestones and score card

Milestones	Y1	Y2	Y3	Y4	Y5
Develop force fields with environment-dependent charges for one metal oxide system.	X				
Perform computational modeling of water gas shift and Fischer-Tropsch reactions.	X	X	X		
Perform computational modeling of PCDD/PCDF production on metal oxide clusters.	X	X			
Develop new force fields and study of additional catalytic processes.		X	X	X	
Validate force field calculations with experimental measurements and DFT calculations.			X	X	X

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