Hydrogen Storage-Relevant Capabilities at Argonne National Laboratories

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Argonne National Laboratory

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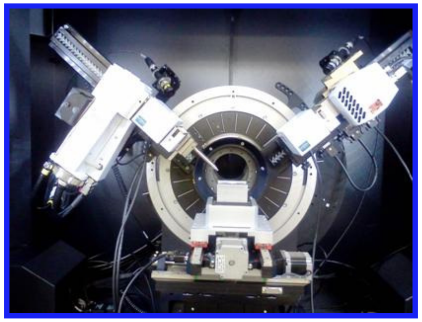
Highlighted cross-cutting capabilities/facilities at ANL

- **High-throughput (HT) Research Lab**
  - Wide range of HT tools for synthesis, characterization, and evaluation of new materials
  - Two robotic systems for exploring a wide range of compositional phase space (Capable of handling air- and moisture-sensitive compounds)
  - X-ray diffractometer designed to integrate seamlessly with HT equipment
  - Two "MGI"-type projects focused on fuel cell material development funded by FCTO. A similar arrangement can be made for H_2 consortium.

Robotic System – Air- and Moisture-Sensitive Synthesis

- **Synchrotron X-ray Characterization (and other User Facilities)**
  - Advanced Photon Source: brightest storage hard X-ray beams in the Western Hemisphere
  - Wide range of techniques applicable to H_2 storage materials characterization: X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), small-angle X-ray scattering (SAXS), and X-ray pair-distribution function (PDF)
  - We are the member of a collaborative access team that operates the Sector 10 beamline with direct access to beamline without need for a "General User Proposal"
  - Expertise within hydrogen/fuel cell group for *in situ* X-ray characterization
- **Group Facilities for H_2 Storage Studies**
  - Sievert isotherm apparatus
  - Micromeritics 2020 surface analyzer
  - Box ovens & tube furnaces for sample synthesis including MOF/hydride synthesis
  - Planetary ball mills
  - Full range material chemistry lab including Schlenk line, glovebox, etc.
  - Bench-top X-ray fluorescence spectrometer for elemental analysis

Argonne's high-throughput research laboratory (A user facility in the making; T. Krause)

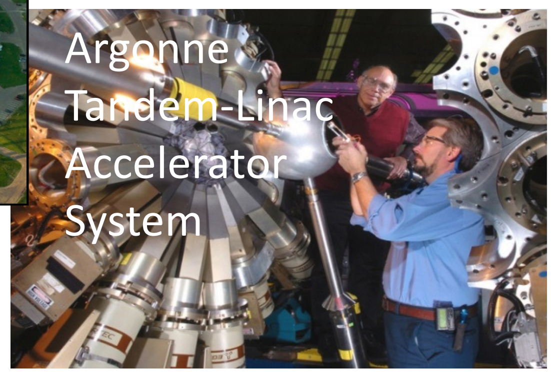


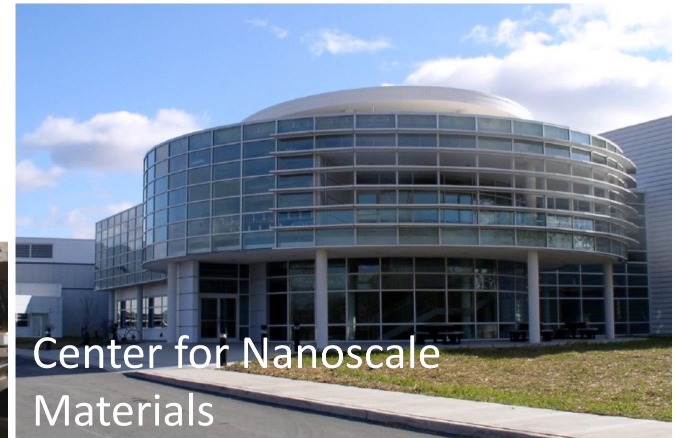
www.cse.anl.gov/pdfs/HTRbrochure.pdf

- Two robotic platform for high-throughput synthesis of materials
  - Robotically-controlled liquid (micro-pipettes) and solid dispensing platform and mixing platforms
- High-throughput apparatuses for heat treatment of materials in a variety of gas atmospheres
- Combinatorial elevated temperature acid treatment of catalyst powders
- Robotic platform for the characterization of materials, solutions, and off-gas generated during heat treatment using:
    - powder X-ray diffraction;
    - gas chromatography with mass spectrometry and flame ionization detectors;
    - liquid chromatography-mass spectrometry
    - dynamic light scattering
    - dc conductivity
- Sixteen parallel plug flow reactors which can be heated up to 900 °C under a variety of gas atmospheres and pressurized up to 1160 psig which are equipped with real-time analysis of gas phase effluent
  - Forty-eight pressure reactors for material screening, material treatment, and process optimization at temperatures up to 400 °C, pressures up to 3000 psig, and under a wide range of gas compositions
  - Computer software to facilitate high-throughput experimental design, data mining, and evaluation of results

Argonne User Facilities


Advanced Photon Source


Argonne Tandem-Linac Accelerator System


Center for Nanoscale Materials

Argonne Leadership Computing Facility


Transportation Research and Analysis Computing Center

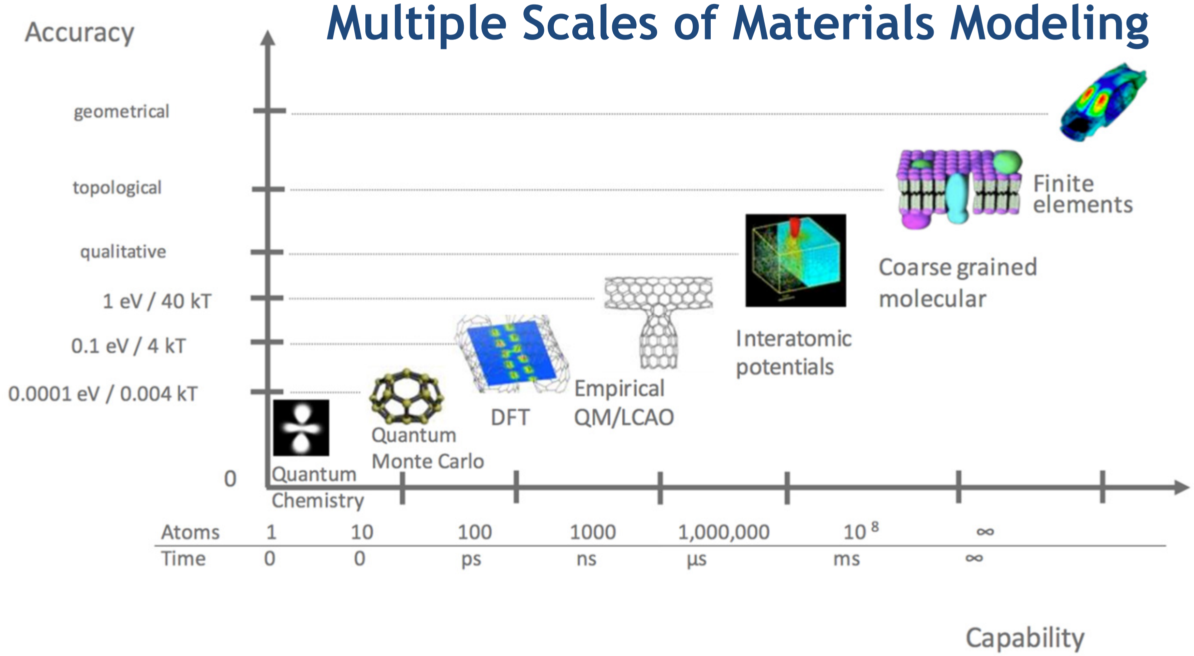

Electron Microscopy Center

Argonne Leadership Computing Facility: Mira – 10PF IBM Blue Gene/Q Supercomputer

Mira Specs

- 1,024 Nodes per Rack
- 1.6 GHz 16-core processors
- 4 Hardware Thread per Core
- 16 GB RAM per Node
- 384 I/O Nodes
- 240 GB/s Network
- 48 Racks
- 786,432 Cores
- 768 Terabytes of Memory
- Peak of 10 petaFLOPS
- 35 PB of Storage
- #5 on Nov 2015 Top500 List

Multiple Scales of Materials Modeling



First principles to microstructural-mechanical property models for predictive modeling

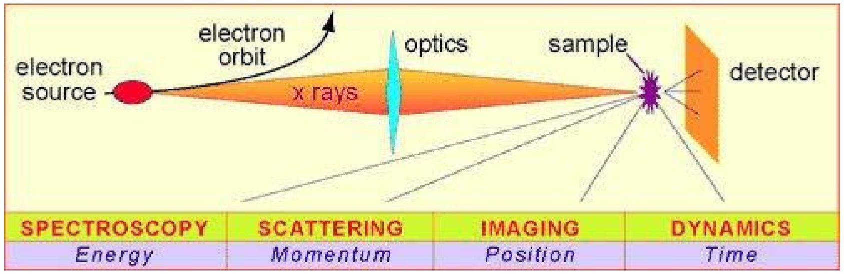
Center for Nanoscale Materials (CNM) and Electron Microscopy Center (EMC)

- **Electronic & Magnetic Materials & Devices:** Synthesis of materials, characterization via STM, DSC/TGA, UHV techniques, etc.
- **Nanobio Interfaces:** Synthesis of metal oxide, semiconducting, magnetic, and metal nanoparticles
- **Nanofabrication and Devices:** Clean room, electron and ion beam lithography, chemical vapor deposition
- **Nanophotonics:** Time-resolved spectroscopies
- **Theory & Modeling:** Carbon High-Performance Computing Cluster, DFT and KMC codes, etc.
- **X-Ray Microscopy:** The Hard X-Ray Nanoprobe (HXN) facility provides scanning fluorescence, scanning diffraction, and full-field transmission and tomographic imaging capabilities with a spatial resolution of 30 nm over a spectral range of 6-12 keV; Full-Field Transmission Imaging and Nanotomography; Scanning Fluorescence X-Ray Microscopy; Scanning Nano-diffraction and Bragg Ptychography
- **Electron Microscopy Center:**
  - ACAT: Argonne Chromatic Aberration-corrected TEM
  - FEI Tecnai F20ST TEM/STEM
  - Zeiss 1540XB FIB-SEM
  - FEI CM30T — analytical transmission electron microscope (AEM)
  - Hitachi S-4700-II — high-resolution, high-vacuum SEM
  - FEI Quanta 400F — high-resolution environmental and variable-pressure SEM

X-ray techniques at the Advanced Photon Source

- Spectroscopy
  - Energy-dependence of absorption; characteristics of chemical bonding and electron motion, no crystallinity required
  - X-ray absorption spectroscopy, X-ray emission spectroscopy, X-ray photon correlation spectroscopy, XPS

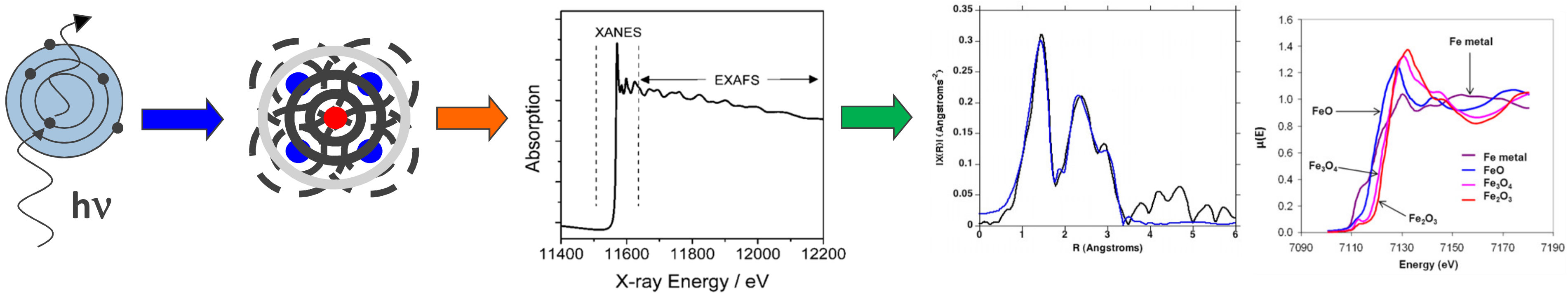
WWW.ANL.APS.GOV



- Scattering
  - Elastic
    - ➢ Particle, agglomerate structure, and ordered atomic structure
    - ➢ Small-angle X-ray scattering, ultra-small angle X-ray scattering, wide-angle X-ray scattering, grazing incidence small angle X-ray scattering, X-ray reflectivity, X-ray diffraction
    - ➢ Pair distribution function
  - Inelastic
    - X-ray Raman Scattering, resonant inelastic X-ray scattering
    - Nuclear resonant X-ray scattering

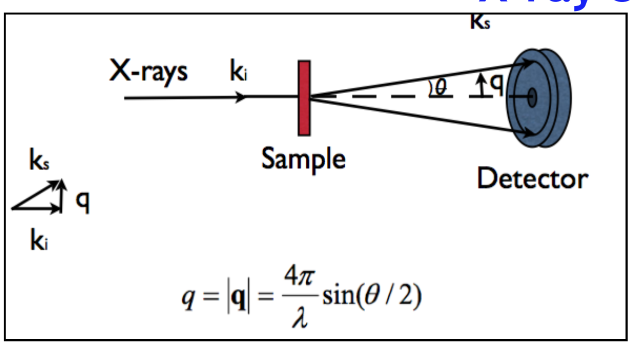
- Imaging
  - Pictures with fine spatial resolution
  - Tomography
  - Nano-fluorescence imaging
  - Phase contrast imaging
  - Radiography
  - X-ray microscopy
  - X-ray photoemission electron microscopy

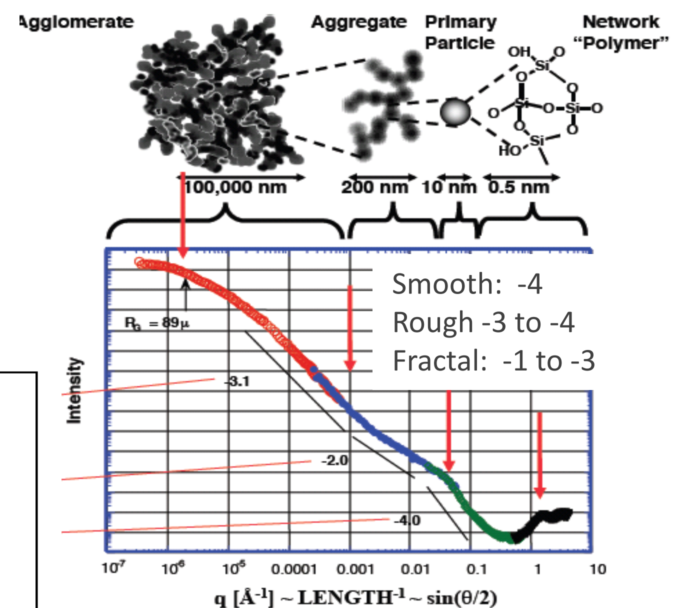
X-ray Absorption and Scattering



- XANES region: sensitive to oxidation state, electronic structure, and local coordination of absorbing atom
- EXAFS region: coordination number, identity of neighboring atoms, and bond distances

X-ray Scattering





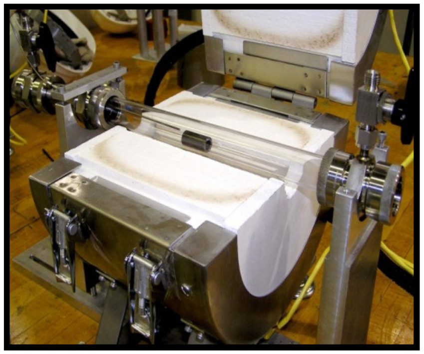
- Particle/aggregate shape, size, size distribution
- Averages over large areas, yields absolute number and volume fraction of particles, and provides time resolution (unlike TEM)
- Everything in beam path scatters
  - Must accurately subtract "background"

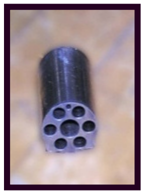
Source: Dale W. Schaefer, University of Cincinnati

XAFS during materials preparation

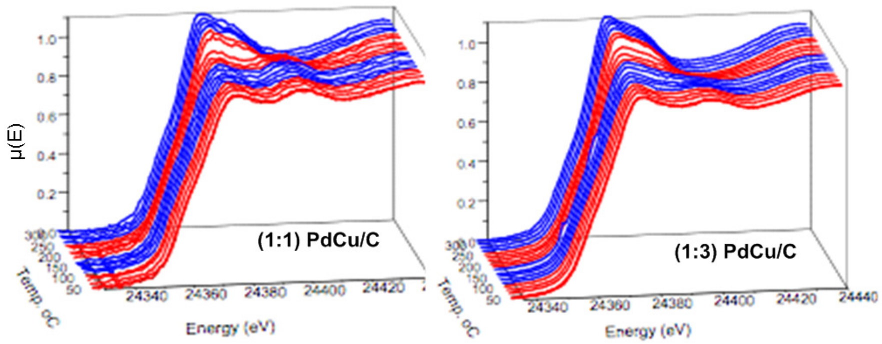
- Transmission XAFS in controlled atmosphere and at elevated temperatures (up to 1000°C)
- Examples:
  - During heat treatment step of materials preparation
  - During temperature-programmed oxidation, reduction, or reaction . Gas analysis via on-line mass spectrometer

Six sample holder

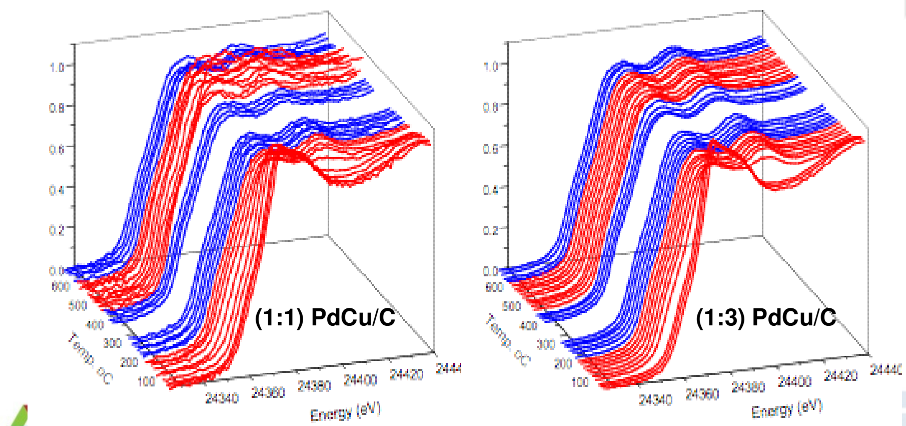


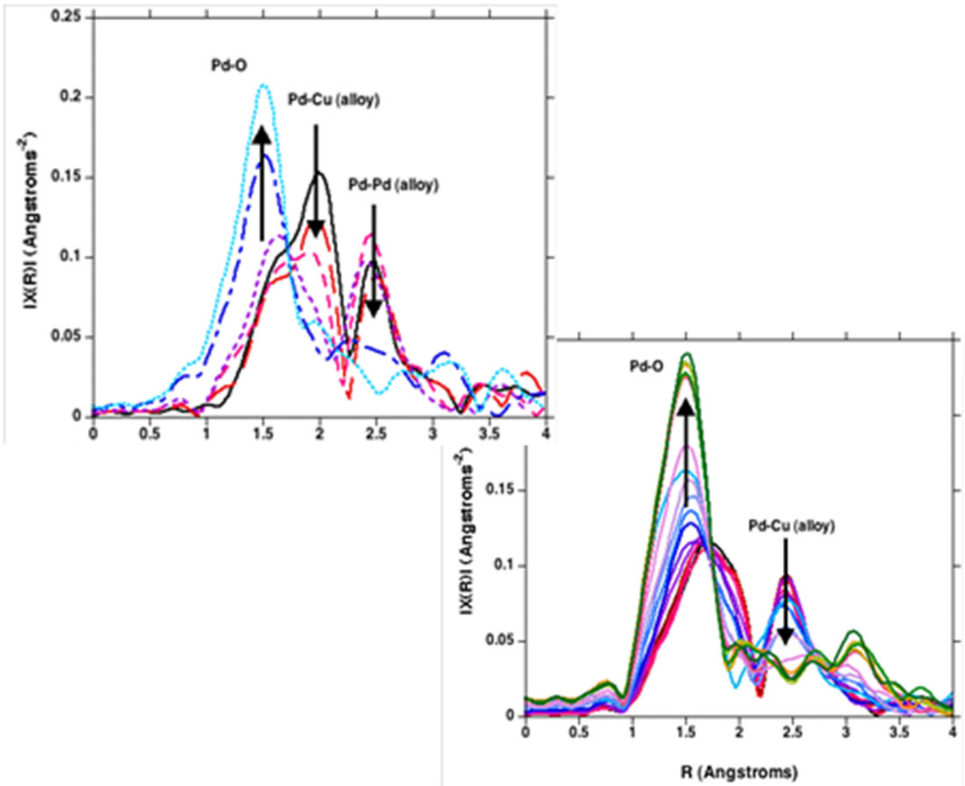


Temperature-programmed oxidation



Temperature-programmed reduction





X-ray scattering, pdf, and diffraction

- **Pair distribution function**
  - Information about materials morphology such as atomic bond lengths and average particle diameter

Example**: In situ XRD data for ball milled MgH_2–5 mol % $V_{75}Ti_5Cr_{20}$.**
C. Ren, et al., J. Phys. Chem. C 118 (38), 21778-21784 (2014).

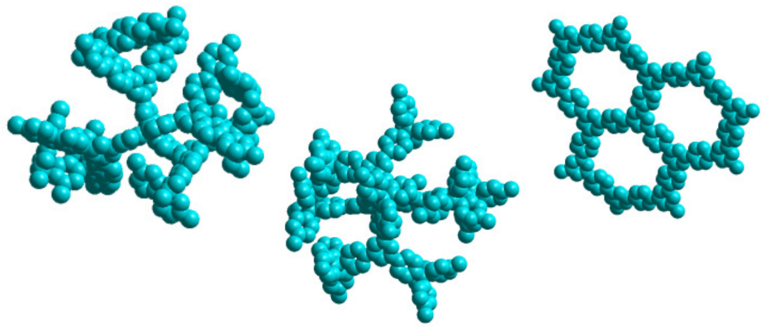
- **Wide angle X-ray scattering (WAXS) and HR-XRD**
  - Crystallographic composition and strain/stress in bulk and at interfaces with 1 μm resolution
  - Can be performed at pressures up to 30 **GPa** and at elevated temperatures (@APS Sector: HP-CAT)

Example: **WAXS of a chromia-poisoned SOFC cathode**.
D.J. Liu and J. Almer, ECS Transactions, 16(51) (2009) 107-113.

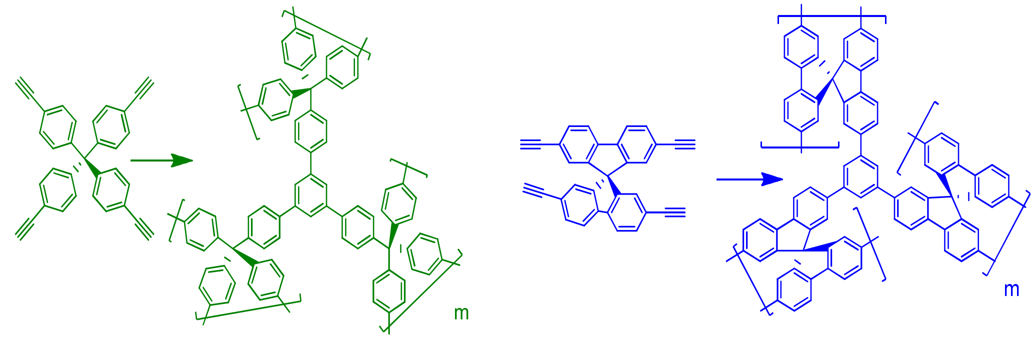
Example: **XRD patterns at various pressures for Li_3AlH_6.**
R.S. Kumar et al., Chem. Phys. Lett., 460 (2008) 442-446.

Aromatic POPs - understanding the effects of molecular structure and pore-size on H_2 sorption

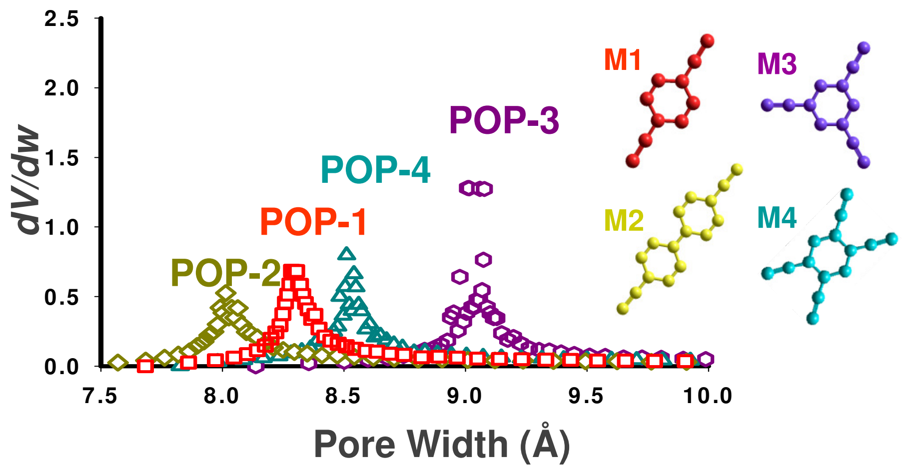
3-D structures of aromatic POPs…



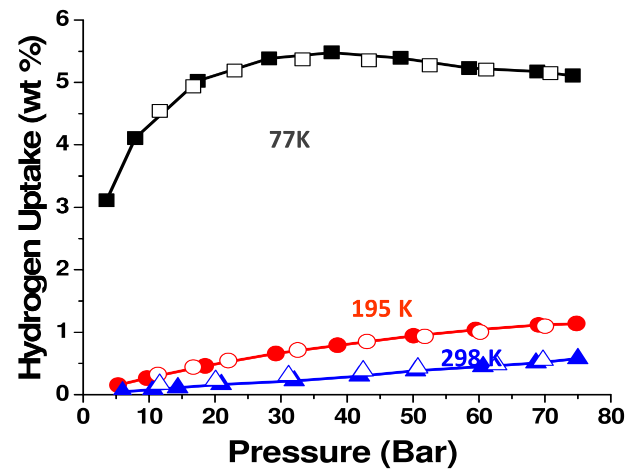
…formed by crosslinking with contorted core…



… with tunable surface area and porosity…



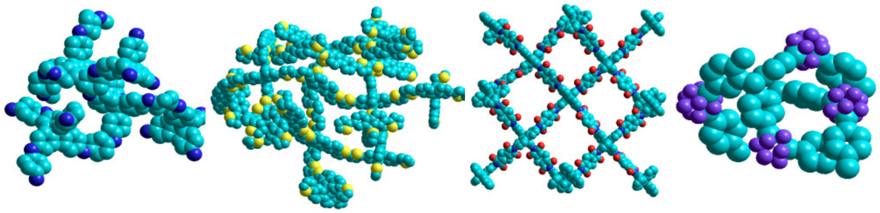
… and are capable of high H_2 uptake …



- Over 50 aromatic POPs were prepared, high BET surface areas (> 3200 m^2/g) and tunable pore sizes (7Å to 10Å) achieved.
- H_2 uptakes up to 5.5% at 77K and 0.5% at RT were achieved, heat of adsorptions are usually limited at ~6 kJ/mol.
- High SSA leads to higher gravimetric hydrogen uptake at 77 K, but not necessarily higher volumetric uptake.

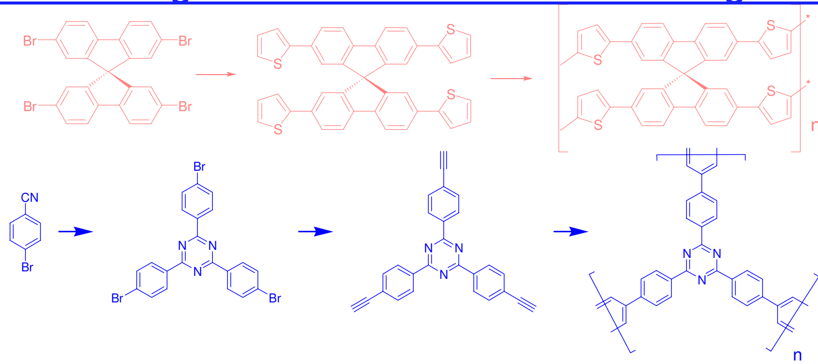
Heteroaromatic POPs - understanding the effects of surface electronic property modification on H_2 sorption

POPs containing non-C elements ...

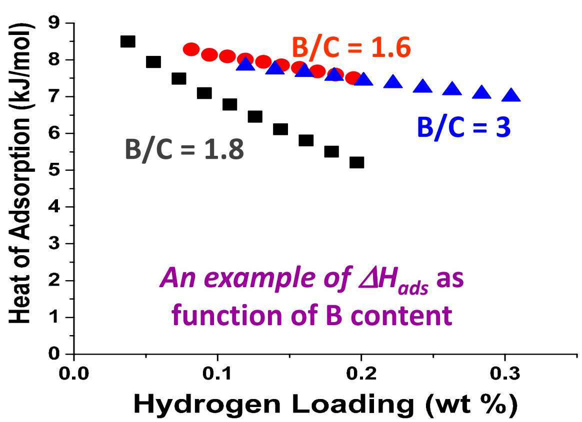


Nitrogen Sulfur Oxygen Boron

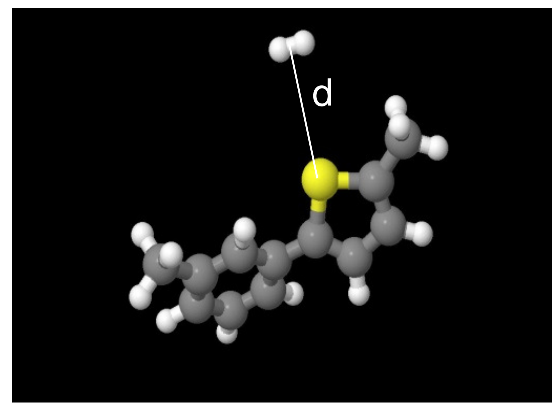
... can be synthesized using various monomers and crosslinking schemes...



...H2 adsorption enthalpy is element-sensitive ...



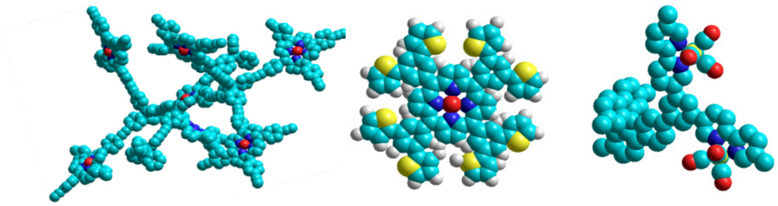
...supported by computational modeling



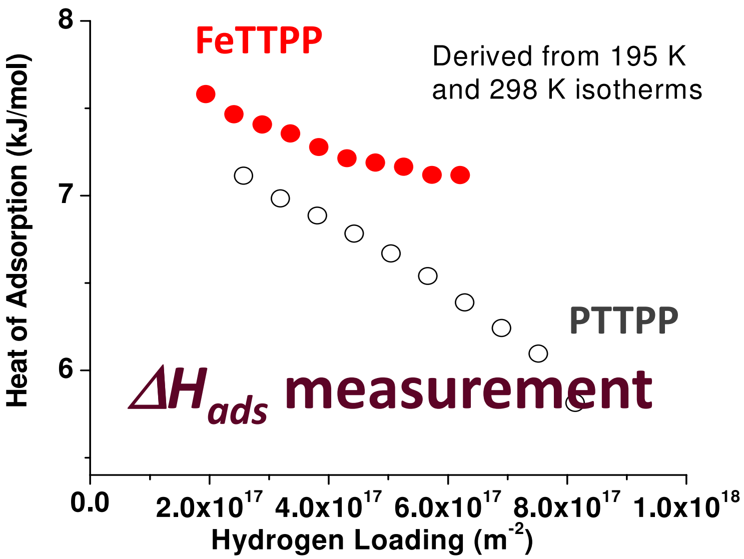
- Over 30 heteroaromatic POPs were prepared containing B, N, S, etc., high BET surface areas (> 2000 m^2/g) and narrow pore sizes (~8Å) achieved.
- H_2 uptakes ~ 4% at 77K and the heat of adsorptions higher than ~9 kJ/mol were achieved.
- Improvement of ΔH_{ads} could be element-dependent, for example, S and N → ΔH_{ads}↓, B → ΔH_{ads}↑

Metallated POP synthesis and hydrogen adsorption strength

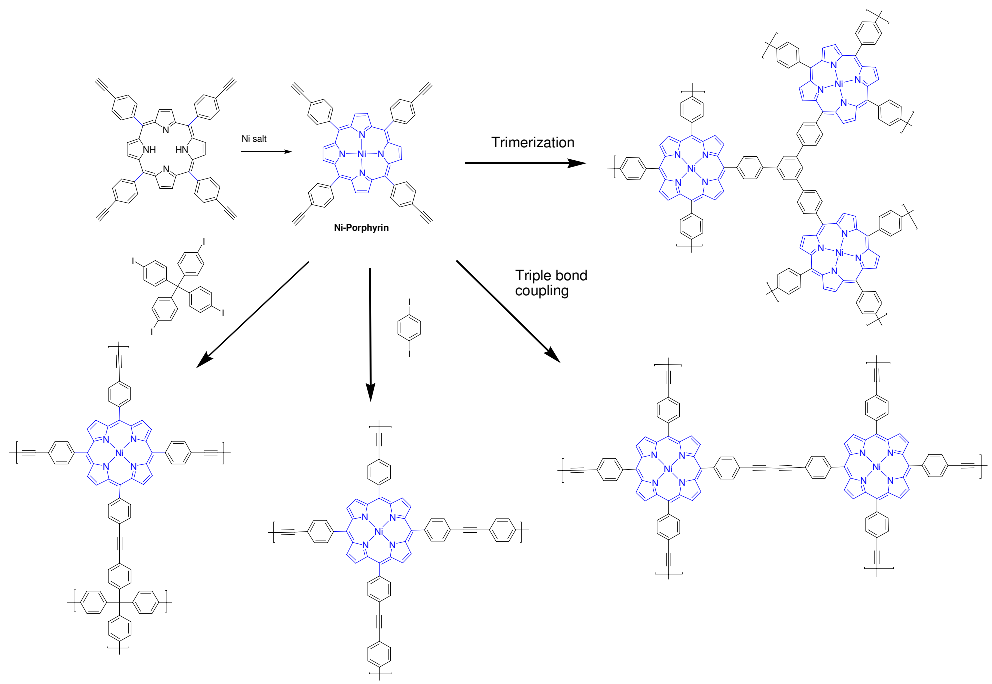
POPs with different TM-ligand coordination were prepared …



… To study metal induced hydrogen binding

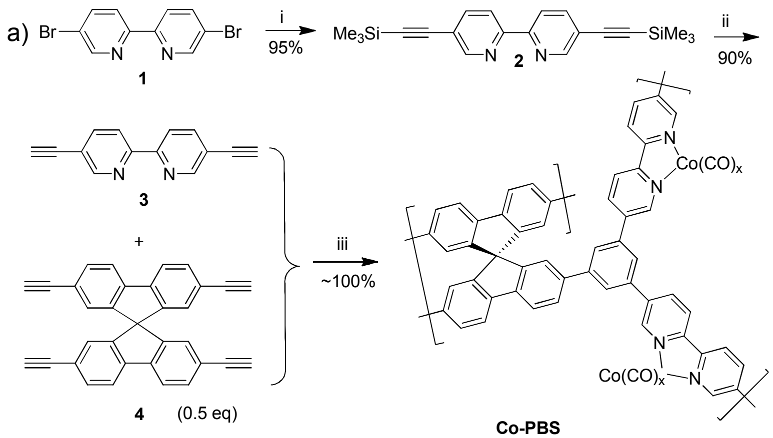


Synthetic Scheme for different M – Polyporphyrins

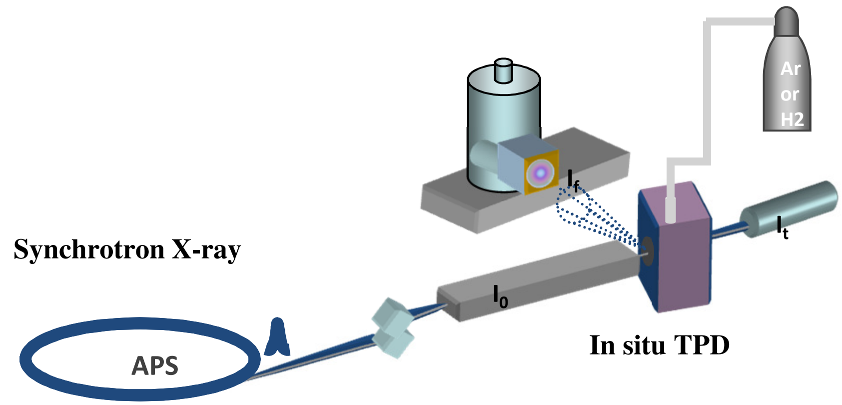


- Over 25 transition metal (Fe, Co, Ni...) doped POPs were prepared with high BET surface (~2800 m^2/g) and narrow pore sizes (~8Å)
- H_2 uptakes of ~ 5.5 % at 77K and the heat of adsorptions as high as ~ 10 kJ/mol were achieved.
- Incorporating TMs clearly improves the isosteric heat of adsorption. New metals (Ti, Mg, V, etc.). Improvements are needed to enhance ΔH_{ads} to the 15 ~20 kJ/mol range.

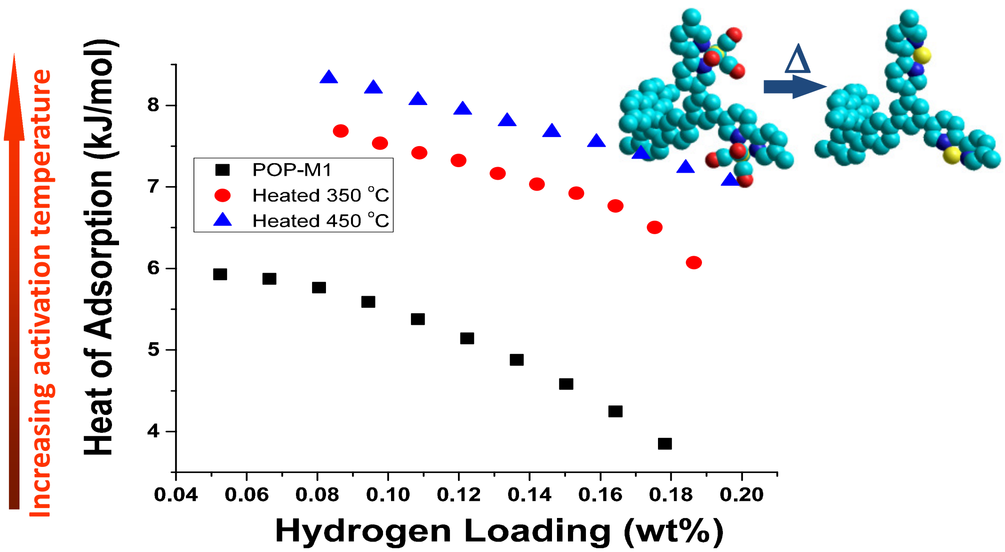
Case study – understanding H_2-TM interaction from synthesis to characterization

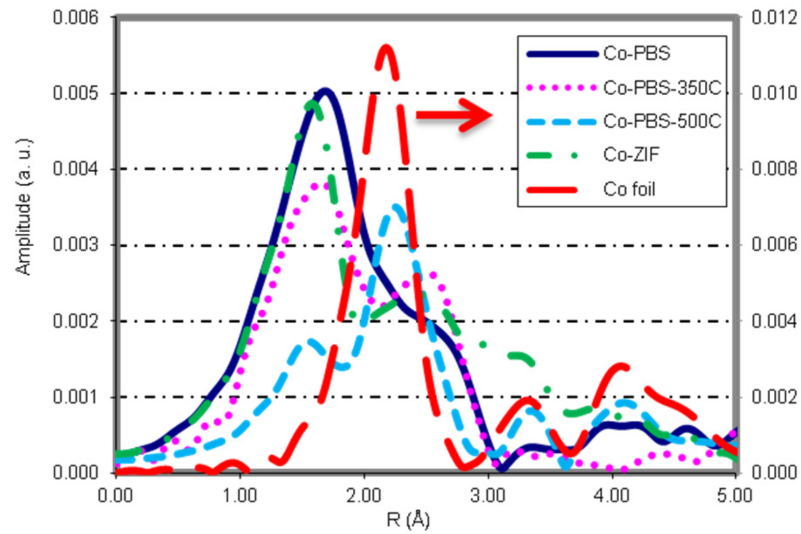


Synchrotron X-ray absorption spectroscopy revealed exposed metal site after thermal activation



Decapping led to formation of coordinatively unsaturated site





S. Yuan, et al., Macromolecular Rapid Communications 33, 407-413 (2012). DOI: 10.1002/marc.201100797

Hydrogen Storage Modeling Activities at ANL

ANL has developed and is using models to analyze the on-board and off-board performance of physical and material-based automotive hydrogen storage systems

- Conducting independent systems analysis for DOE to gauge the performance of H_2 storage systems
- Providing results to material developers for assessment against system performance targets and goals and help them focus on areas requiring improvements
- Providing input for independent analysis of costs of on-board systems.
- Identifying interface issues and opportunities, and data needs for technology development
- Performing reverse engineering to define material properties needed to meet the system level targets

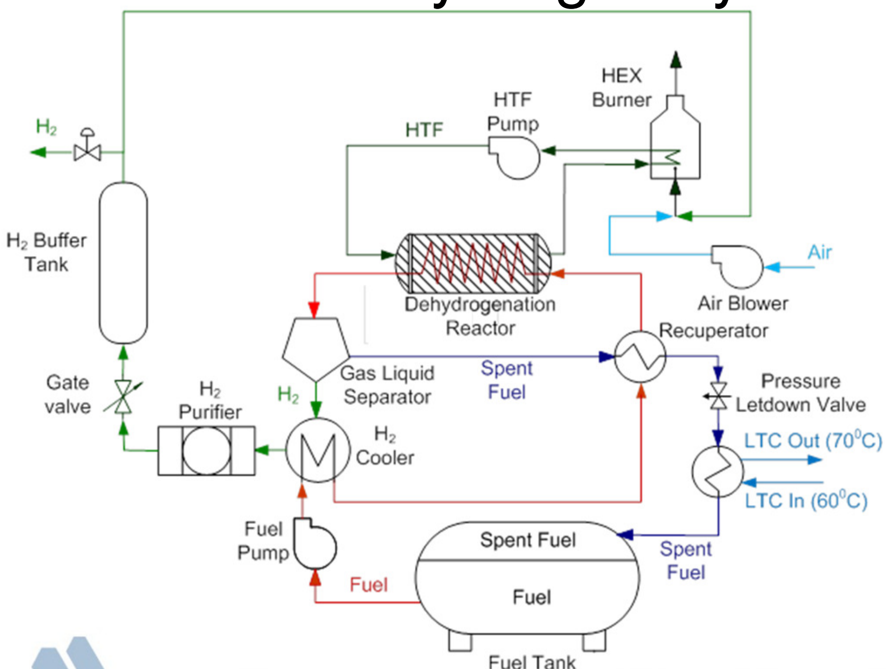
Methods and Tools for System Analysis

- Physical, thermodynamic and kinetic models of all processes. Rigor of analysis to resolve system-level issues, conduct trade-off analyses and provide fundamental understanding of system/material behavior
- Benedict-Webb-Rubin equation of State: REFPROP coupled to GCtool
- High pressure storage tank performance analysis with ABAQUS
- Hydrogen uptake in sorbents: Ono-Kondo, DA isotherms, Gibbs potential
- Dynamic models for gaseous/liquid refueling, discharge, dormancy
- Reactor models with heat transfer, mass transfer, recycle
- Engineering flowsheets with industrial processes for off-board regeneration
- FCHtool for efficiency, H2A for hydrogen production and component models, HDSAM for H_2 delivery scenario analysis
- For consistency, vehicle performance targets (range, peak supply rate, minimum/maximum delivery pressure, refueling time, cycle life) treated as constraints

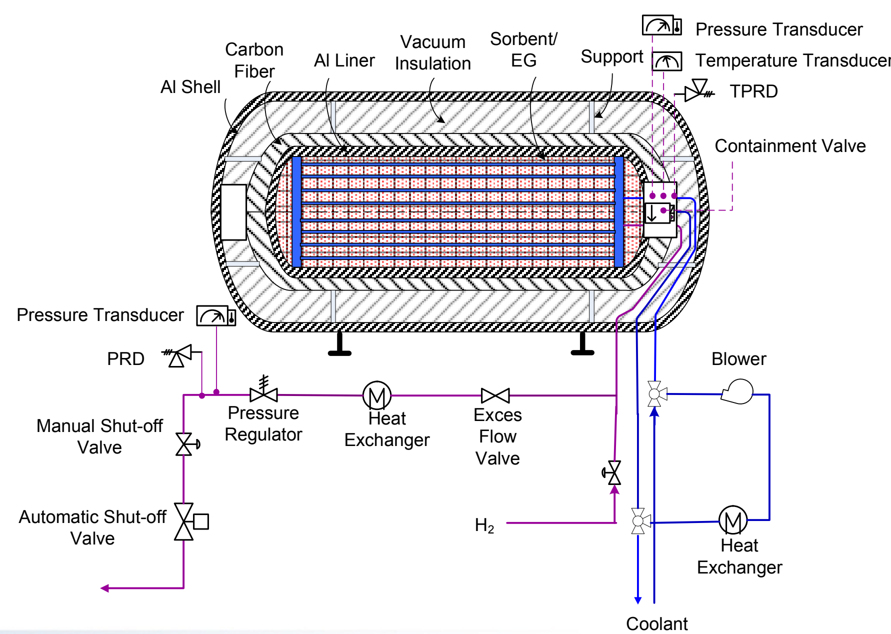
Material-Based Hydrogen Storage System Analysis

- **On-board attributes**
  - Gravimetric and volumetric capacity on usable H_2 basis
  - System efficiency
  - System cost at high-volume manufacturing
  - Other performance targets (range, peak supply rate, minimum/maximum delivery pressure, refueling time, cycle life)

Chemical hydrogen system



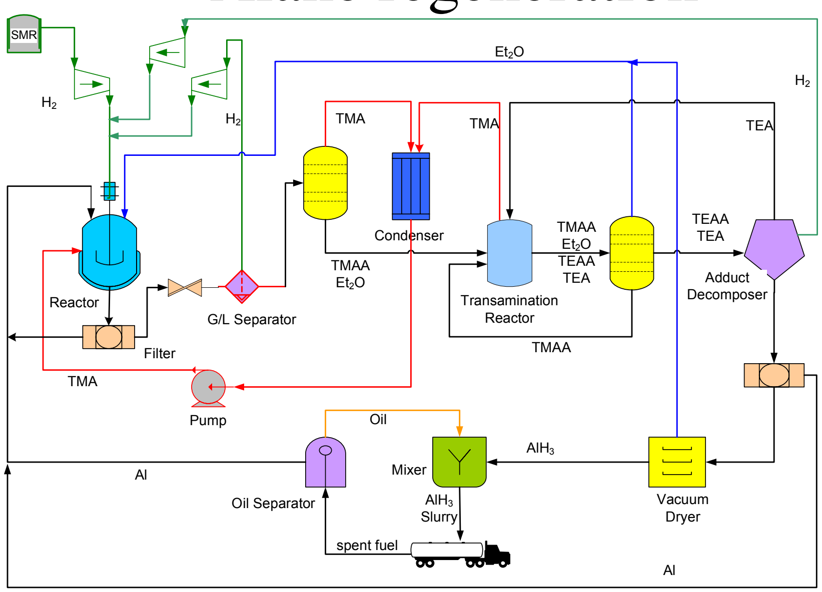
Sorbent system



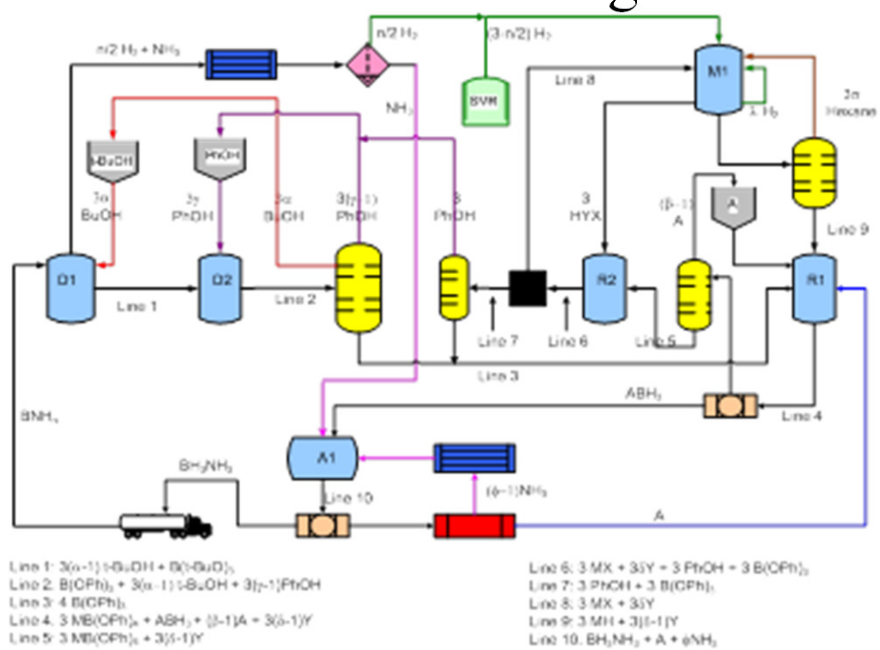
Off-Board Regeneration Analysis

- **Off-board attributes**
  - Process energy and optimization
  - Regeneration efficiency with utilization of industrial waste heat
  - Well-to-tank (WTT) efficiency
  - GHG emissions (kg-CO_2 equivalent/kg-H_2)
  - Cost

Alane regeneration



Ammonia borane regeneration



Argonne's Hydrogen Storage Research Capabilities

- **Materials synthesis**
  - Metal-organic frameworks, porous-organic polymer, nanoparticles
  - High-throughput robotic system to facilitate rapid synthesis and screening
- **Materials characterization**
  - Hydrogen uptake and desorption
  - Heats of adsorption
  - Physical, chemical, and structural properties, in situ, ex situ, high-throughput characterization using robotic system
- **Fundamental interactions**
  - First principles to microstructural properties
  - Extensive computational facilities for materials modeling and visualization
- **Material and system engineering and analysis**
  - Kinetics and thermodynamics of all processes, system capacities, efficiencies, regeneration/re-fueling, system lifetime

Examples of Hydrogen Storage Research at the APS

M.H. Braga, A. El-Azab, "The catalytic reactions in the Cu–Li–Mg–H high capacity hydrogen storage system," Phys. Chem. Chem. Phys. 16 (42), 23012-23025 (2014). DOI: 10.1039/C4CP01815J

Hyunjeong Kim, Kouji Sakaki, Yumiko Nakamura, Etsuo Akiba, "Understanding hydrogen storage properties of metal hydrides using the atomic pair distribution function," J. Hydro. Energy Sys. Soc.-- Japan 37, 308-313 (2012).

Ravhi S. Kumar, Xuezhi Ke, Andrew L. Cornelius, Changfeng Chen, "Effect of pressure and temperature on structural stability of potential hydrogen storage compound Li_3AlH_6," Chem. Phys. Lett. 460 (4-6), 442-446 (2008). DOI: 10.1016/j.cplett.2008.06.038

Ravhi S. Kumar, Eunja Kim, Andrew L. Cornelius, "Structural Phase Transitions in the Potential Hydrogen Storage Compound KBH[subscript 4] under Compression," J. Phys. Chem. C 112, 8452-8457 (2008). DOI: 10.1021/jp0765042

Ravhi S. Kumar, Xuezhi Ke, Jianzhong Zhang, Zhijun Lin, Sven C. Vogel, Monika Hartl, Stanislav Sinogeikin, Luke Daemen, Andrew L. Cornelius, Changfeng Chen, Yusheng Zhao, "Pressure induced structural changes in the potential hydrogen storage compound ammonia borane: A combined X-ray, neutron and theoretical investigation," Chem. Phys. Lett. 495 (4-6), 203-207 (2010). DOI: 10.1016/j.cplett.2010.06.044

Chai Ren, Z. .Zak Fang, Chengshang Zhou, Jun Lu, Yang Ren, Xiaoyi Zhang, "Hydrogen Storage Properties of Magnesium Hydride with V-Based Additives," J. Phys. Chem. C 118 (38), 21778-21784 (2014). DOI: 10.1021/jp504766b

S. Yuan, D. White, A. Mason, B. Reprogle, M. Ferrandon, L. Yu, and D-J Liu, "Improving Hydrogen Adsorption Enthalpy through Coordinatively Unsaturated Cobalt in Porous Polymer", Macromolecular Rapid Communications 33, 407-413 (2012). DOI: 10.1002/marc.201100797

Publications related to metal-organic framework and porous organic polymer synthesis and characterization

Shengwen Yuan, Desiree White, Alex Mason, and Di-Jia Liu, "Porous Organic Polymers Containing Carborane for Hydrogen Storage", *Int. J. of Energy Research*. **2013**, 37 (7) 732-740.

Zhuo Wang, Shengwen Yuan, Alex Mason, Briana Reprogle, Di-Jia Liu, and Luping Yu, "Nanoporous Porphyrin Polymers for Gas Storage and Separation", *Macromolecules* **2012**, *45* (18), pp 7413–7419

Chi-Kai Lin, Dan Zhao, Wen-Yang Gao, Zhenzhen Yang, Jingyun Ye, Tao Xu, Qingfeng Ge, Shengqian Ma, and Di-Jia Liu, "Tunability of Band Gaps in Metal-Organic Frameworks", *Inorg. Chem.* **2012**, 51, 9039–9044

S. Yuan, D. White, A. Mason, B. Reprogle, M. Ferrandon, L. Yu, and D-J Liu, "Improving Hydrogen Adsorption Enthalpy through Coordinatively Unsaturated Cobalt in Porous Polymer", *Macromolecular Rapid Communication*. **2012**, *33,* 407–413

Shengwen Yuan, Brian Dorney, Desiree White, Scott Kirklin, Peter Zapol, Luping Yu and Di-Jia Liu, "Microporous Polyphenylenes with Tunable Pore Size for Hydrogen Storage", *Chem. Comm*. **2010**, 46, 4547 – 4549

J. Xia, S. Yuan, Z. Wang, S. Kirklin, B. Dorney, D-J Liu and L. Yu, "Nanoporous Polyporphyrin as Adsorbent for Hydrogen Storage", *Macromolecules*. **2010,** 43, 3325–3330.

S. Yuan, S. Kirklin, B. Dorney, D.-J. Liu and L. Yu, "Nanoporous Polymers Containing Stereo-contorted Cores for Hydrogen Storage", *Macromolecules* **2009**, 42(5), 1554-1559