Hydrogen Storage-Relevant Capabilities at Argonne National Laboratories

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This presentation does not contain any proprietary or confidential information
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 H₂ consortium.

• **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 H₂ 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 H₂ 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

- **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

[Image of X-ray scattering diagram]
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

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

- **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: **In situ XRD data for ball milled MgH₂–5 mol % V₇₅Ti₅Cr₂₀.**

Example: **WAXS of a chromia-poisoned SOFC cathode.**

Example: **XRD patterns at various pressures for Li₃AlH₆.**
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 H₂ sorption

POPs containing non-C elements... ...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 m²/g) and narrow pore sizes (~8 Å) achieved.
- H₂ 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 m²/g) and narrow pore sizes (≈8Å)
- H₂ uptakes of ≈ 5.5 % at 77K and the heat of adsorptions as high as ≈ 10 kJ/mol were achieved.
- Incorporating TMIs clearly improves the isosteric heat of adsorption. New metals (Ti, Mg, V, etc.). Improvements are needed to enhance ΔHₐₚ to the 15 ~20 kJ/mol range.

**ΔHₐₛ measurement**

- Derived from 195 K and 298 K isotherms
- Heat of Adsorption (kJ/mol)

<table>
<thead>
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<th>Hydrogen Loading (m⁻²)</th>
<th>ΔHₐₛ (kJ/mol)</th>
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</thead>
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<td>8.0x10⁻¹⁷</td>
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<tr>
<td>4.0x10⁻¹⁷</td>
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</table>

- FeTTPP
- PTTPP
Case study - understanding H₂-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

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 H₂ 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 H₂ 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 H₂ 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-CO₂ equivalent/kg-H₂)
  - 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


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


