HIGH-THROUGHPUT/COMBINATORIAL TECHNIQUES IN HYDROGEN STORAGE MATERIALS R&D WORKSHOP

U.S. Department of Energy
Office of Hydrogen, Fuel Cells and Infrastructure Technologies

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On June 26, 2007, DOE's Hydrogen Storage Program held a one-day High-Throughput/Combinatorial Techniques in Hydrogen Storage Materials R&D meeting to identify how to better implement high-throughput/combinatorial techniques to benefit research on advanced hydrogen storage materials. Participants represented industry, academia, and national laboratories.

The objectives of this meeting were to:

- Assess the potential for high-throughput/combinatorial methods to benefit and accelerate hydrogen storage materials R&D
- Identify the advantages and disadvantages of the application of high-throughput/combinatorial techniques to hydrogen storage materials R&D
- Match high-throughput/combinatorial techniques with specific types of hydrogen storage materials
- Identify the technical challenges and limitations associated with applying these techniques to hydrogen storage materials R&D
- Recommend appropriate "next steps," if any, to advance the application of these techniques to hydrogen storage materials

BREAKOUT SESSIONS SUMMARIES

Following the technical presentations, three breakout groups were formed based on material types – adsorbents, chemical hydrogen storage materials, and metal hydrides. Each breakout group was asked to consider the following for their type of hydrogen storage material:

- List the potential classes of materials;
- List the high-throughput/combinatorial method(s) appropriate for the specific material type;
- Consider the availability and state of technology development of the methods listed above;
- List the advantages/disadvantages of the identified methods and the technical challenges or gaps that must resolved for each method;
- Identify the next steps for implementing the methods.

Summaries of the discussions in each of the breakout group follow-

<u>Adsorbents (led by Carole Read)</u>

State of development for high-throughput technology:

(a) Synthesis.

In general, liquid-phase synthesis methods are highly developed and it was concluded that they could be used for high-throughput studies on a variety of adsorbent material classes. For example, these processes have been used for metal organic framework (MOF) synthesis with success. They are also amenable to air/water-free conditions. It was concluded that the technical risk would be low in applying liquid-phase methods to other adsorbent materials.

(b) Testing.

A critical need is the development of high-throughput characterization/testing methods that are proxies for H_2 uptake measurement. In fact, this capability would be of great value to all three material types considered in this workshop. One example being attempted is the use of solvent uptake as an indicator of surface area. The amount of solvent absorbed could be an indicator of the surface area available for sorption.

Six classes of materials were discussed:

1. Metal Organic Frameworks (MOFs)

For MOFs, it was indicated that the "success" rate for synthesizing promising crystalline materials is low. Synthesis is solution-based with solids handling similar to proven combinatorial methods. Exploration of new structures should benefit from combinatorial methods and result in a rapid increase in discovery rate. Characterization methods discussed include X-ray diffraction (XRD), surface area by solvent uptake, Raman with solvent uptake, color chromic sensing, and multiple thermogravimetric analysis (TGA)/temperature programmed desorption (TPD) (high-throughput techniques need development).

2. Dopants/Catalysts for Adsorbent Materials

High-throughput synthesis could be done by vapor infiltration (similar to heterogeneous catalyst synthesis). Proposed characterization methods include surface area measurements, small angle X-ray scattering (SAXS) to determine pore size (needs development), hydrogen uptake measurements (high-throughput techniques need development).

3. High Surface Area Porous Inorganic Materials

Synthesis techniques include electrochemical, solid handling, and supercritical drying methods. Suggested characterization approaches include pore size and distribution techniques (high-throughput techniques need development).

4. Polymers

Synthesis approaches include grafting, cross-linking, pyrolysis, radical and Atom Transfer Radical Polymerization (ATRP). Synthesis also includes metal incorporation and solids handling. Suggested characterization methods include SAXS, pore size distribution, molecular weight distribution, hydrogen uptake and surface area measurements (high-throughput techniques need development).

5. Aerogels

Synthesis is based on standard sol-gel processes and should be similar to heterogeneous catalysts synthesis. Combinatorial methods should yield a rapid rate of discovery if coupled with surface area measurements. Suggested characterization approaches include pore size distribution (an important parameter for these materials) measurements. This measurement technique would likely need to be developed for high-throughput application.

6. Nanostructures

High-throughput synthesis may be difficult due to the metastable nature of many nanostructures and the very process-dependent synthesis approaches in use. Rapid nuclear magnetic resonance (NMR) was a proposed characterization technique that might be amenable to high-throughput analysis (high-throughput techniques need development).

Synthesis and characterization/testing of adsorbent materials lend themselves to high-throughput/combinatorial methods due to the large number of variables. The emphasis in research needs should be on characterization (especially for MOFs to find the best performers and eliminate further study of the others) but high-throughput rapid synthesis techniques can also play an important role. Both synthesis and characterization methods need to be explored and developed and applied to a variety of materials, particularly metal doped/bridged adsorbents.

<u>Metal Hydrides (led by Ned Stetson)</u>

The discussion in this group was limited to H_2 in and out of the tank (off-board regeneration was not considered) and to light-weight materials. To meet the DOE system gravimetric targets it was noted that only light elements, such as early alkali-alkaline earth metals (ex. Li, Na, Mg, Ca), semi-metals (ex. B, Al, Si) and non-metals (ex. C, N, P) may be used with only small quantities of transition metals. In addition to the "composition-space" limitation, it was recognized that the sorption properties of some metal hydride materials may be significantly affected by impurities (or contaminants) and this should be a consideration when selecting screening methods. A lengthy discussion took place concerning the relevance of thin/thick film testing of potential metal hydride materials compared to bulk materials testing. Due to the limited number of elements and the concern over relevance of thin film metal hydride materials to bulk metal hydride materials, it was thought that high-throughput screening methods may not be necessary for reversible metal hydride materials discovery but that medium-throughput methods might be appropriate. High-throughput screening of catalysts was not discussed; however, it is recognized that catalysts may play an important role in the development of a successful metal hydride material system to meet DOE targets and high-throughput screening methods may be very beneficial in this area.

Various high to medium-throughput synthesis methods were considered. Methods for continuous and discrete phases for thin and thick film formation were identified. These processes included: pulsed laser deposition (PLD); activated chemical vapor deposition (CVD); sputtering; molecular beam epitaxy (MBE); and electron-beam deposition.

Methods for screening bulk materials included: solvent-based processing; ball milling (micro-milling); melt or near-melt processing; and hot sintering (micro-hot plate).

The advantages and disadvantages for high-throughput methods of thin and thick films were discussed. For thin films the identified advantages included: many compositions are possible; rapid screening possible and less material is required. The disadvantages to thin films are that: the sample may not be representative of bulk material properties (sample relevance) and the results may not scale up to bulk accurately. For thick films, the advantages identified included:-minimal surface area; minimal interface issues; improved structure (i.e. more relevance to bulk materials) and relaxation of strain. The disadvantages included: delamination of the film from the substrate; texturing of the sample and potential columnar growth that, in some cases, may not be typical of bulk material structure.

Likewise, the advantages and disadvantages of micro-milling were discussed. Identified advantages included: milled material is representative of bulk material with enhanced surface area; it is a proven technique for synthesizing materials; it is simpler to scale-up for material production; and there is a wide diversity of reagents for possible use. The disadvantages included that it is not as high-throughput as other processing techniques and there is a greater potential for sample contamination.

A number of characterization methods for metal hydride materials that might be amenable to high-throughput/combinatorial analysis were identified: These methods included: calorimetry (nano-calorimetry); nuclear analytical methods (such as Prompt Gamma Activation Analysis (PGAA), Nuclear Activation Analysis (NAA) and Neutron Diffraction); optical methods (such as Infrared Spectroscopy (IR) and Thermography); gas detection; gravimetric methods; electrical resistivity; volumetric methods and secondary ion mass spectroscopy (SIMS). Participants agreed that such methods are useful for rapid qualitative screening rather than rigorous quantitative characterization of capacity.

<u>Chemical Hydrogen Storage (led by Grace Ordaz)</u>

High-throughput synthesis and characterization of chemical hydrogen storage materials is not a critical issue because a large number of promising materials have been identified and additional materials can be readily synthesized via the traditional material formulation methods. However, the search for effective catalysts to enhance kinetics and selectivity for both hydrogen release and for regeneration chemistry could benefit greatly from high-throughput screening techniques. Examples of potential rapid screening catalyst studies include:

- Automated and high-throughput initial screening of catalysts, including combinations/permutations of catalysts, for hydrogen release.
- Automated optimization of additives (both accelerants and inhibitors).
- Automated screening of catalysts for reaction selectivity for both hydrogen release as well as for regeneration of spent fuel.
- Screening of homogeneous and heterogeneous catalysts.

High-throughput techniques and capabilities exist commercially that provide initial catalyst screening to detect hydrogen release. Automated sampler and characterization equipment provide "medium-throughput" catalyst data regarding selectivity/desired reaction pathways.

Micro-reactor techniques are used to screen catalysts that will provide the necessary reaction kinetics. Especially for heterogeneous catalyst systems, the micro-reactors need to be customized to the appropriate reactor configurations to obtain accurate data. These screening micro-reactors can be readily and custom built both in-house and by commercial entities, but are costly.

Issues that were identified included:

- Cost of the necessary equipment.
- The required "back-end" automated analysis tool (i.e., characterization) may be a bottleneck.

Conclusions/Next Steps

A common theme resulting from this workshop was the need for high-throughput/combinatorial characterization and testing methods for hydrogen uptake and/or release for all material types. The input of the participants will be used by the DOE EERE Hydrogen Storage Team to structure future programmatic plans toward the development of hydrogen storage materials that have the potential to meet or exceed the DOE performance targets. Depending on budgetary constraints, it is possible that a future solicitation may ask for proposals dealing with the development of high-throughput/combinatorial approaches for the synthesis and characterization/testing of hydrogen storage materials. Although theoretical computational techniques as a high-throughput tool were not covered in this workshop, recent experience has shown that theory-guided approaches combined with experimental validation providing feedback to the theoretical work can be an effective approach for the identification and development of viable storage materials. Thus, theory/experimental approaches are highly recommended.

Participants are encouraged to continue to communicate their ideas, suggestions and comments on high-throughput/combinatorial approaches for hydrogen storage materials to the DOE team and to other researchers in the science and engineering community.