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**FUEL CELL**  
REVIEW

Volume 3 Issue 3 June/July 2006

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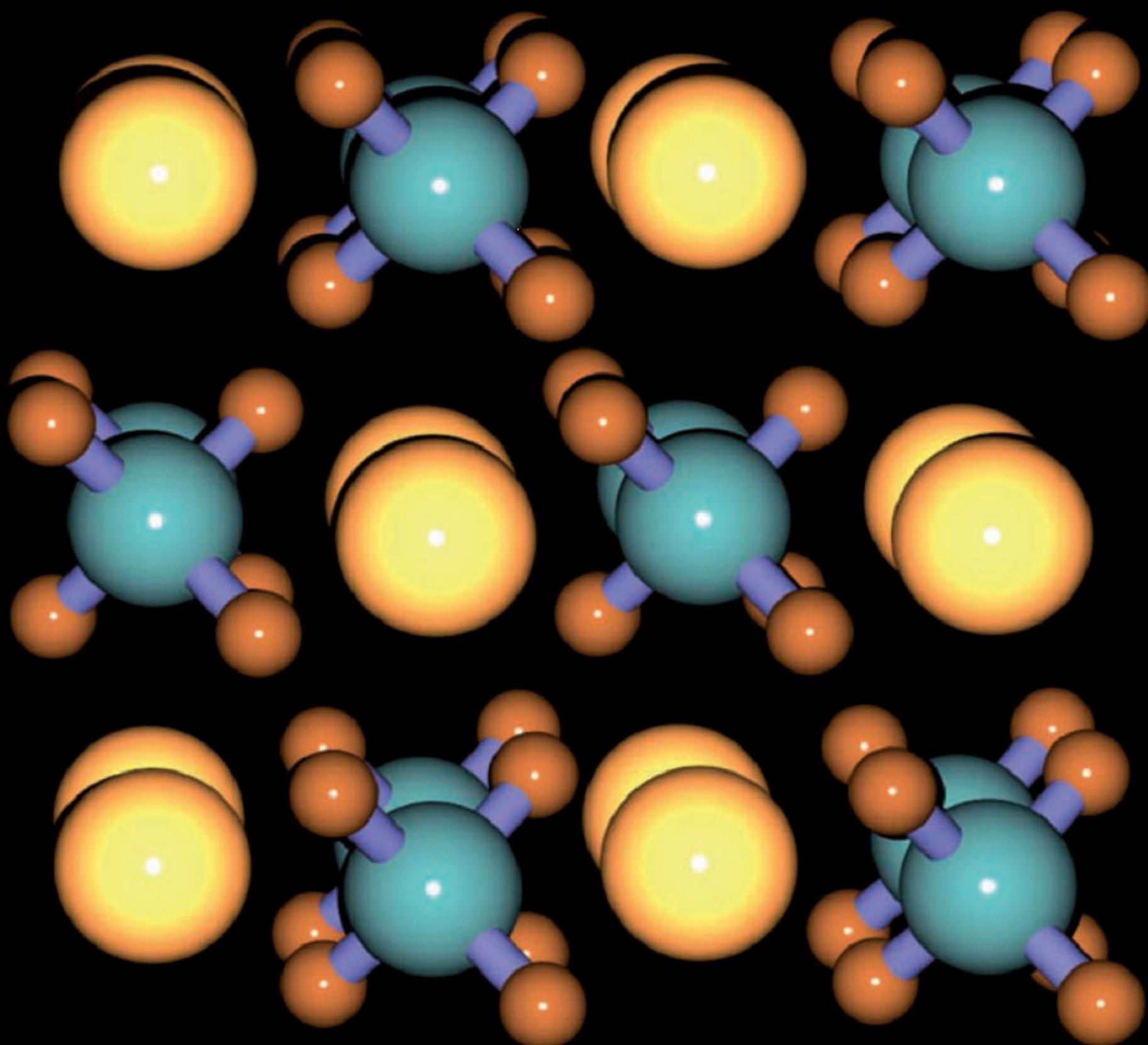
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# On-board storage and metal hydrides



# An evolving strategy on hydrogen storage

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**An ambitious US research collaboration wants to develop a safe, economical hydrogen-storage system based on reversible metal hydrides.**

HYDROGEN-STORAGE materials are potentially the most attractive option for both in-vehicle and stationary applications, though researchers first need to make serious inroads on a daunting hit-list of fundamental scientific and technological challenges. Assuming that they do, the ideal storage material will one day combine a high wt% of hydrogen and high volume density; the ability to absorb (or adsorb) and desorb hydrogen at, or close to, room temperature and at pressures around 1 bar; and rapid absorption (or adsorption) and desorption kinetics. At the same time, this ideal store will be made from cheap, readily available materials using a straightforward and low-energy method of preparation. It will in turn demonstrate resistance to poisoning by trace impurities, along with good thermal conductivity in charged and uncharged conditions for ready heat management. Last, but not least, it will be safe and reusable on exposure to air and must be easily recyclable.

No such material exists yet – at best it lies on the distant horizon. Reaching that distant horizon, however, is the stuff of the US National Hydrogen Storage Project, a \$150 m five-year plan through which the US Department of Energy (DOE) hopes to realize commercially viable hydrogen-storage materials for stationary and transportation markets. A key strand of this programme, the Metal Hydride Center of Excellence (MHCoe), was established in April 2004 with a remit “to discover and develop efficient, safe and cost-effective reversible hydrogen-storage materials for vehicle applications”. The focus is on advanced metal-hydride materials, including light weight complex hydrides, destabilized binary hydrides, intermetallic hydrides, modified lithium amides, and other reversible hydrides.

## A process of elimination

With this objective in mind, the initiative brings together a team of interdisciplinary US researchers drawn from eight universities, three industrial partners and six national/federal laboratories (see “MHCoe deliverables”, p22). Sandia National Laboratories (Livermore, California) is the lead partner, providing management of the collaboration as well as assisting and advising the DOE on project strategy and progress. The MHCoe’s activities are grouped into five main priorities: 1) materials development and discovery, including rapid experimental development efforts; 2) fundamental modelling and science to understand



**In focus: researchers at Sandia National Laboratories are developing innovative experimental and theoretical techniques to investigate new combinations of metal hydrides as storage materials. Here, Eric Majzoub studies a metal-hydride storage material using a Raman spectrometer with a microscope set-up for analysing samples with a micron-scale probing area.**

hydrogen–materials interaction and to provide direction for the screening efforts; 3) materials synthesis and improved performance through compositional, structural, catalytic and nanosynthesis modification; 4) rigorous testing of hydrogen storage and delivery properties to support fundamental science and timely evaluation of materials research directions; and 5) engineering/process development to accelerate the commercialization of the best hydrogen-storage materials and systems.

Ultimately, all of this collective effort is about meeting or beating the DOE’s 2010 and 2015 targets for on-board hydrogen storage. That means:

- By 2010, researchers are required to develop and verify on-board hydrogen-storage materials achieving storage-system targets of 2 kWh/kg (6 wt%), 1.5 kWh/l, fill time of

## The US National Hydrogen Storage Project

When the DOE issued its Grand Challenge to the scientific community in July 2003, it was asking for nothing less than a fundamental breakthrough on novel materials for hydrogen storage. The Grand Challenge called for the establishment of three hydrogen-storage centres of excellence (metal hydrides, chemical hydrogen storage and carbon-based materials) with multiple university, industry and federal laboratory partners. At the same time, independent projects were solicited on new materials and concepts, off-board hydrogen storage systems, and analyses of life-cycle cost, performance and environmental impact.

The centres of excellence and independent projects constitute the framework of the National Hydrogen Storage Project. This five-year programme, backed by \$150 m in federal funding, has been tasked with the development of hydrogen-storage systems capable of meeting long-

term DOE targets. Complementing the Grand Challenge, the DOE Office of Science issued a solicitation in 2004 for basic research to help overcome key hurdles in hydrogen production, storage and conversion.

The Metal Hydride Centre of Excellence targets the development of advanced metal-hydride materials, including lightweight complex hydrides, destabilized binary hydrides, intermetallic hydrides, modified lithium amides and other on-board reversible hydrides. The Chemical Hydrogen Storage Center of Excellence targets three “tiers” of R&D for chemical hydrogen storage: borohydride–water, novel boron chemistry and innovation beyond boron. The Carbon-Based Materials Center of Excellence targets breakthrough concepts for storing hydrogen in high-surface-area sorbents such as hybrid carbon nanotubes, aerogels and nanofibres, as well as metal–organic frameworks and conducting polymers.

3 min for 5 kg of hydrogen and \$4/kWh.

- By 2015, develop and verify on-board hydrogen-storage materials achieving storage-system targets of 3 kWh/kg (9 wt%), 2.7 kWh/l, fill time of 2.5 min for 5 kg of hydrogen and \$2/kWh.

Lennie Klebanoff, the MHCoe’s newly appointed director, told *The Fuel Cell Review*: “All of the R&D activities are driven by the DOE targets [for on-board hydrogen storage]. As a result, we have set out well defined milestones for the 17 partners involved in the Centre of Excellence. We are advancing with a practical approach that is broad enough to help us find the materials that meet the targets.”

As such, the DOE’s annual merit review of the MHCoe – the latest one was held in May – provides an important reality check on progress to date and the ways in which R&D priorities are evolving and being reprioritized on an ongoing basis. Sandia, for its part, published a raft of new results on Li/X amides, complex hydrides and rapid-assessment hydride modelling. Its progress on LiX amides over the preceding 12 months included the determination of a reaction pathway for  $(2\text{LiNH}_2 + \text{MgH}_2)$ ; quantitative assessment of  $\text{NH}_3$  contamination of desorbed  $\text{H}_2$  from Li/Mg amide (approximately 420 ppm  $\text{NH}_3$  at 220 °C); measurements of extended cycling of Li/Mg amide, which showed that desorption capacity depends strongly on absorption history; and the synthesis and characterization of a new Li-Al-N-H compound. Since the storage capacity of the Li/Mg material seems to be limited to ~5 wt% (well below even the DOE system requirements), Sandia’s report to the merit review concludes that experimental work on Li/Mg amides will be suspended, while other promising amide systems (other than Li/Mg) will be explored. Overall, more emphasis will be given to novel preparations of borohydrides over the next 12 months.

Meanwhile, work on complex hydrides has yielded a major shift in the MHCoe’s longer-term R&D priorities with respect to alanate-based storage materials. Despite early work at Sandia that highlighted encouraging absorption properties, alanates

have been all but ruled out in the race to meet the DOE’s on-board hydrogen-storage targets. “We have found that the alanates do not meet the required targets,” said Klebanoff. “As a result, most of the community is moving from working on alanates to calcium and magnesium borohydrides.”

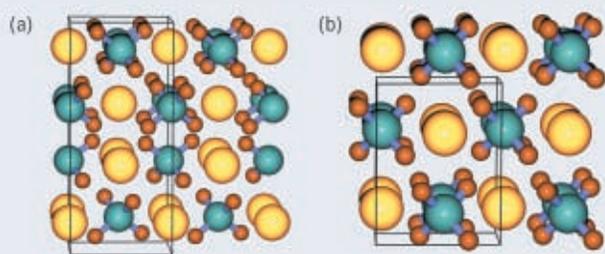
In fact, Sandia’s work over the past 12 months has demonstrated the feasibility of solid-state synthesis of new borohydrides in the Ca-B-H and Mg-B-H systems, as well as the synthesis of several metal borohydrides via solvent-based exchange reactions. Klebanoff added: “We are stepping up our research into borohydrides due to their high theoretical storage weight capacity. If alanes [ $\text{AlH}_3$ ] were reversible they would already fit our model of the ideal storage material. On the theoretical front here at Sandia, we have also developed a new approach to generate [crystal] structures for potential materials.”

Throughout the MHCoe, researchers evaluate candidate materials using a “go/no-go” process of elimination, with progress checked quarterly against milestones. However, finding the right storage material is, in Klebanoff’s view, not such a black-and-white process: “We do not want to simply single out any particular material. Even the negative results we have found thus far have provided positive theoretical insight.” At the same time, Klebanoff says that he is well aware that the DOE targets necessitate “practical resource-allocation decisions”.

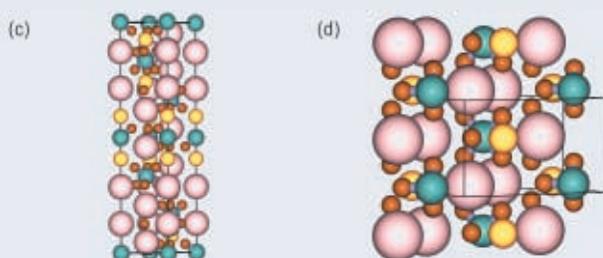
Put another way: as some avenues of research close, others open. In this regard, Sandia’s Eric Majzoub and colleagues are pioneering a new take on the modelling of complex metal hydrides. Their approach uses Monte Carlo energy minimization of electrostatic forces followed by quantum-mechanical calculations to estimate the reaction enthalpies of promising candidate materials. “The biggest advantage of our electrostatic model is that it is easy for me to generate structures for mixed cation materials, and to do this rapidly,” said Majzoub.

The Monte Carlo method has been validated on known systems (sodium alanate and a bialkali alanate). For example, by treating sodium alanate as an ionic solid, dominated by electrostatics, the researchers then generated different potential

## 1. High-throughput hydride modelling



Sandia researchers are pioneering a new take on the modelling of complex metal hydrides. Their approach uses quantum-mechanical Monte Carlo calculations to estimate the reaction enthalpies of promising candidate materials. The Monte Carlo method has been validated on known systems like sodium alanate. (a) The known crystal structure of sodium alanate, originally established in the early 1980s (*J. Inorg. Chem.* 1983 28 1528). (b) A Monte Carlo structure generated by Sandia's Eric Majzoub and Vidvuds Ozolins at UCLA. Sodium atoms (yellow), aluminium (green) and hydrogen (brown).



Sandia's Monte Carlo technique has been used to predict crystal energies of complex quaternary hydrides. (c) Sandia scientist Ewa Ronnebro synthesized  $K_2LiAlH_6$ , a bialkali alanate, and found its crystal structure using experimental means. (d) A corresponding Monte Carlo structure, calculated by Majzoub and Ozolins, has a first-principles total energy only a few tens of meV above the ground state of the experimental structure. Potassium atoms (pink), lithium (yellow), aluminium (green) and hydrogen (brown).

theoretical structures for the storage material. "We input information about the cations and complex anions, and, given the same input structures using the Monte Carlo technique, we minimize the electrostatic energy to generate different output structures," explained Majzoub. "We are aiming to decipher the crystal-structure energies in order to determine the approximate enthalpy of formation."

Majzoub continued: "The advantage of our technique is that we don't require any knowledge of the crystal structure to obtain an estimate of the enthalpy. The other approach to getting the crystal-structure energy is to go to a crystal-structure database and select structures and calculate their energies, but this is a random hit-or-miss approach."

Majzoub's team has used the Monte Carlo method to calculate the heat of formation of calcium borohydride, with results indicating proper stability. Further quantum-mechanical calculations – including lattice vibrations, yield pressure versus temperature curves – show that calcium borohydride, and the closely related magnesium borohydride, may be reversible at practical pressures and temperatures. At Sandia, these quantum-mechanical calculations have been performed by Roland Stumpf. Sandia has been joined in the theoretical effort by Duane Johnson at the University of Illinois at Urbana-Champaign and Karl Johnson at the University of Pittsburgh.

### The power of partnership

As with Sandia, other MHCoe partners also reported significant progress in the DOE's merit review. General Electric (GE), for example, has developed a robust combinatorial/high-throughput screening tool for faster discovery of new hydrides and catalysts. "The tool allows us to synthesize and evaluate multiple compositions simultaneously, instead of one composition at a time," said J C Zhao, team leader for hydrogen storage at GE.

Zhao and his colleagues have also developed a high-pressure apparatus to allow *in situ* X-ray diffraction study of the hydriding and dehydriding reactions. Using this set-up, the scientists can reveal the mechanism by watching the hydrogen interaction/reaction with metals *in situ* with changing temperature and pressure. "We have used the tool to study several hydrides systems that were developed at Sandia, HRL [Hughes Research Laboratory] and GE," added Zhao.

Meanwhile, HRL has been busy tackling two of the major challenges associated with light-metal hydrides for reversible hydrogen storage: strong metal-hydrogen bonds that lead to low equilibrium pressures and prohibitively slow rates of hydrogen exchange. "We're addressing the thermodynamics challenge through the use of hydride destabilization strategies in which alloy or compound formation in the dehydrogenated state reduces the overall energy for the reacting system, resulting in a increase in equilibrium pressure," explained HRL's Greg Olson, team leader for the MHCoe's destabilized systems project. Although a system that meets all of the thermodynamic requirements has yet to be demonstrated, "hydride destabilization provides a compelling approach to developing a materials system that meets those goals," Olsen added.

The kinetics challenge is perhaps even more daunting. On this front, HRL is exploring approaches that employ nanoscale materials to reduce diffusion distances, thereby increasing rates for hydrogen exchange. "We're investigating methods for incorporating metal-hydride reactants into nanoporous 'scaffold' structures (e.g. carbon aerogels)," said HRL researcher John Vajo. "Confinement of the metal hydride within the scaffold host has been shown to improve kinetics. More work is needed, though, to optimize the scaffold and to incorporate hydride destabilization agents into the framework."

Elsewhere, hydride synthesis is the number one priority. Zak Fang and colleagues at the University of Utah, for example, have developed two separate techniques for the synthesis of metal hydrides: one uses a high-energy, high-pressure reaction

## MHCoE deliverables come into focus

The MHCoE addresses the technical barriers defined by the on-board hydrogen storage section of the DOE's hydrogen, fuel cells and infrastructure technologies multiyear research, development and demonstration plan:

- **Cost:** low-cost materials/components are needed for hydrogen-storage systems and low-cost, high-volume manufacturing methods.
- **Weight and volume:** materials/components are needed to allow compact, lightweight hydrogen-storage systems while enabling a range over 300 miles in all light-duty vehicles. Thermal management components with reduced weight/volume are a priority.
- **Efficiency:** the energy required to get hydrogen in and out of the material is an issue for reversible solid-state materials. Optimization is needed for thermal management for charging/releasing hydrogen from the system.
- **Durability:** materials/components must support hydrogen-storage systems with a lifetime of 1500 cycles and tolerance to fuel contaminating substances.
- **Refuelling time:** there is a need to develop hydrogen-storage systems with refuelling times of less than 3 min for 5 kg of hydrogen over the lifetime of the system. Thermal management during refuelling needs to be addressed.

With these priorities in mind, the MHCoE brings together a partnership between universities, national laboratories and industrial firms with Sandia serving as lead laboratory and coordinator of the collaborative R&D efforts.

**Sandia National Laboratories:** MHCoE management; development of complex anionic materials; development of amide materials; storage-bed engineering; theory and theory coordination.  
**General Electric:** synthesis and *in situ* characterization of metal

hydrides and their absorption/desorption.

**Hughes Research Laboratory:** synthesis of destabilized metal hydrides; structural and chemical characterization.

**Caltech:** synthesis of nanoparticle materials for hydrides.

**Jet Propulsion Laboratory:** nuclear magnetic resonance investigations of metal hydrides; hydride-bed storage engineering.

**University of Hawaii:** metal hydride synthesis and characterization.

**University of Pittsburgh:** theoretical investigations of hydride absorption and desorption.

**Carnegie Mellon University:** theoretical investigations of hydride absorption and desorption.

**University of Illinois at Urbana-Champaign:** electron microscopy characterization of metal hydrides; theoretical studies.

**University of Utah:** synthesis of amide materials and complex anionic materials.

**Intematix:** combinatorial studies of metal hydrides.

**National Institute of Standards and Technology:** neutron diffraction studies of hydrogen absorption.

**Oak Ridge National Laboratory:** hydride synthesis.

**University of Nevada-Reno:** lifetime and cycling studies of amides/imides; materials reliability; *in situ* X-ray diffraction and neutron studies during cycling.

**Savanna River National Laboratory:** engineering studies for metal-hydride tanks; molten-state synthesis of hydrides, alanes.

**Brookhaven National Laboratory:** alanes synthesis and characterization.

**Stanford University:** thermodynamically tuned nanophase materials for reversible hydrogen storage; structure and kinetics of nanoparticle and model system materials.

milling technique; the other a chemical-vapour synthesis (CVS) process. Among the materials they are working on, a combined system of lithium amide with lithium hexahydroaluminat has what Fang describes as “a very high potential as a storage material”. The material system, which has up to 7 wt% reversible hydrogen storage capacity at moderate temperature, was prepared by a custom-designed high-energy milling process. “Nanosized aluminium powder produced by the CVS process will be used to prepare this and other aluminium-containing hydrogen-storage materials,” added Fang.

Aluminium hydride ( $\text{AlH}_3$ ) is also shaping up as a promising material for solid-state hydrogen storage, according to Jim Wegrzyn, team leader on the alanes MHCoE project at Brookhaven National Laboratory (BNL). Unlike the stable chemical hydrides and reversible metal hydrides,  $\text{AlH}_3$  is trapped in a thermodynamically metastable state. “The advantage of using such a metastable hydride is that considerably less heat is required for decomposition, which reduces the need for a complex heat exchanger system in the hydride tank,” Wegrzyn explained. In addition,  $\text{AlH}_3$  has a volumetric hydrogen density (0.148 g/ml) greater than that of liquid hydrogen, a gravimetric hydrogen capacity exceeding 10 wt% and can supply hydrogen

at temperatures below 100 °C. The snag, says Wegrzyn, is that “ $\text{AlH}_3$  cannot be recharged on-board the vehicle because of thermodynamic barriers. Currently, the BNL programme is focused on the development of a novel, efficient and economically attractive off-board recharging process.”

### Chasing down those targets

To date, the MHCoE's progress looks encouraging. That said, the project partners have taken only the first small steps on the long road to finding the ideal hydrogen-storage material. The task for Klebanoff and his colleagues is to keep on delivering the fundamental innovations and breakthroughs that will inform ongoing reprioritization of the R&D roadmap for light-metal hydrides. If they can do that, they'll be hoping for a little bit of luck or genius or both, to hit upon the radical big idea that changes the game for everyone working towards the ultimate goal of sustainable hydrogen fuel-cell vehicles. ●

• For further information about the MHCoE, visit [www.ca.sandia.gov/MHCoE/](http://www.ca.sandia.gov/MHCoE/)

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