

IV.C.1 DOE Hydrogen Sorption Center of Excellence

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- Create a collaborative, nimble environment to permit expeditious exploration, research, and deployment (sum of whole > sum of parts).
- Enable new storage system concepts possible with “smart” materials to meet DOE system targets (e.g. conformal tanks with low temperature [T] and moderate pressure [P] <100 bar operation using hybrid nanoengineered systems with near standard temperature and pressure operation).

Technical Barriers

The Hydrogen Sorption Center of Excellence (HSCoE) is developing novel high-surface area materials and systems for on-board vehicle hydrogen storage. The CoE presently has thirteen active projects at twelve institutions and anticipates the start of two new projects at ANL and MUOhio. HSCoE partners are conducting a wide range of applied research and engineering studies on currently available adsorbent materials and developing design principles and synthetic methods for next generation materials that will meet the critical DOE 2010 system hydrogen storage targets. The technical barriers address by these projects from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, include:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

The HSCoE is developing materials to meet the DOE FY 2010 Hydrogen Storage system targets. Lists of representative HSCoE experimental results to date are provided in Table 1.

Accomplishments

The HSCoE partners worked closely together to systematically accelerate the development of advanced hydrogen sorbent materials. Representative accomplishments are listed below.

Objectives

- Investigate a variety of adsorbent materials known to store hydrogen to determine limits of performance.
- Design and synthesize materials that bind hydrogen reversibly as either (i) weakly bound atoms or (ii) as strongly bound molecules.
- Understand possible mechanisms and the interplay between structure, binding, and material and storage densities (volumetric and gravimetric).
- Develop the experimental and computational tools to speed discovery, testing, and deployment of new materials that meet DOE system goals.

TABLE 1. Progress Towards Meeting Technical Targets for Hydrogen Storage for Transportation Applications: Experimental Results

Materials Performance																			
Storage Parameters	Units	System Targets (2010)	MOF-177 ^a (UM/UCLA)		Spillover (UM)		SWNTs (NREL)		M-C ₆₀ (NREL)		Aerogels (LLNL)			Pt-SWNH (ORNL)		Reduced Carbons ^d (NREL)		B-doped Carbons ^e (PSU)	
			FY05	FY06	FY05	FY06	FY05	FY06	FY06	FY07	FY06	FY07	FY07	FY06	FY07	FY06	FY07	FY06	FY07
Specific Energy	Wt% H ₂	6	2.5	7	1.6	~4	b	3	0.5	0.5	4.2	5.3	>8 ^e	1	2.5	4.2	5	*	3.2
Volumetric Energy Capacity	g/L	45	*	31	*	41	*	28	*	*	*	29	*	*	*	*	*	*	*
Comments			77 K, 50 bar	77 K, 60 bar	RT, 100 bar	RT, 100 bar		77 K, 20 bar	77K, 2 bar	STP ^g	77 K, 30 bar	77 K, 30 bar	STP ^g	77K, 10 bar	77 K, 10 Bar	STP ^g	STP ^g		77 K, 30 bar

* Information not available

Volumetric capacities derived from material densities

^aWong-Foy et al., JACS 128, 3494 (2006)

^bPrior to 2006, SWNT hydrogen uptake results have not been reproduced at different labs. 4 to 6 wt% results reported.

^cWhen loaded with LiBH₄, the aerogel as a scaffold lowered the desorption temperature to ~400C.

^dMaterials developed at NREL are mostly irreversible since a dissociation component has not yet been incorporated.

^eBoron binding sites demonstrated ~10 KJ/mol, close to theoretical predictions. SSA needs to be increased (~800 m²/g)

^fNote that outside the center, ~5 wt % (77K and 90 bar) and ~8 wt% (77 K and ~100 bar) were demonstrated with MOFs by M. Dinca et al. JACS 128, 16876 (2006) and templated carbons by Z. Yang et. al. JACS 1021/ja067149g (2007), respectively.

^gStandard temperature and pressure.

- Developed a detailed understanding for hydrogenated materials and demonstrated substantial storage at near ambient conditions.
 - Developed mechanistic (APCI and UM) and atomistic (Rice and NREL) models that accurately describe the observed storage mechanisms associated with hydrogen spillover. These results provide a detailed understanding that will enable spillover kinetics and capacities to be increased.
 - Validated previous published spillover results.
 - Spillover results on activated carbon (NREL and UM) and the significantly enhanced capacities observed with bridged IRMOF-8 (UM) were independently validated. Bridged IRMOF-8 material were independently reproduced by a group at the Institute of Nuclear Energy Research (INER) in Taiwan and the 4 wt% storage capacities at room temperatures were validated by the DOE-designated validation laboratory, Southwest Research Institute (SwRI).
 - NREL demonstrated the ability for carbon materials (activated carbon and single walled nanotubes [SWNTs]) to store substantial quantities of hydrogen at ambient conditions via hydrogenation with reduced binding energies.
- Synthesized new hydrogen storage materials with enhanced hydrogen binding energies and the potential for high storage capacities.
 - LLNL developed carbon aerogels (CA) with large pore volumes (up to 2.7 cm³/g) and used them as a “nanoscaffold” in the preparation of a CA/LiBH₄ nanocomposite that exhibited over 8 wt% H₂ desorption and showed a decrease in hydrogen desorption temperature relative to bulk LiBH₄. This work was performed in collaboration with Metal Hydride CoE members at HRL Laboratories.
 - LLNL synthesized materials with the highest surface areas ever achieved for the specific material (e.g. CAs at 3,200 m²/g and single walled carbon nanotube scaffolded fibers)
 - PSU and NREL synthesized boron-doped (up to ~8 at% B using PSU boron-containing precursors) porous carbon structures that demonstrated 10 to 12 kJ/mol isosteric heats of adsorption (as measured by NIST and UNC) and reasonable specific surface areas.
 - NREL synthesized new organometallic fullerene compounds with unique hydrogen adsorption sites.
 - Caltech synthesized metal-organic frameworks (e.g. MOF 74 and MIL-53) and other structures that showed higher than expected uptake on the basis of specific surface area. Some of these materials demonstrated adsorption/desorption hysteresis that is an indication of capillary condensation well above the condensation temperature for hydrogen.

- Preliminary studies using polyaniline materials synthesized by Penn indicated ~2.8 wt% hydrogen uptake at 77 K.
- Rice created 3-D nanoengineered carbon nanotube frame for direct hydrogen uptake and as a scaffold for metals for room temperature binding. This involved developing expansion methods for spun fiber and cross-linking methods to make rigid scaffold and specifiable pore spacings. The synthesized scaffolds exhibit a two time steeper slope for H₂ uptake than Chahine's rule which extrapolates to 6.5 wt% uptake.
- Duke developed methods to prepare microporous carbon materials with controllable pore sizes using different surfactants as organic templates. The average pore size (~1.2 nm) will be decreased to less than 1 nm and dopants will be introduced to optimize the materials to meet DOE hydrogen storage targets.
- NREL designed and identified several new materials via computational engineering which show the potential to meet DOE hydrogen storage system targets. Several of these promise to be more readily synthesized and more stable than previously found organometallic bucky balls.
 - Metallaboranes: B₆₀Sc₂₀H₁₄₄) ~8.6 wt%, reversible, 52 kgH₂/m³
 - Metallocarboranes: (C₃B₂)₁₂Ti₁₂H₁₃₂) ~8.6 wt%, reversible, 43 kgH₂/m³ and (C₃B₂)₁₂Sc₁₂H₁₄₄ : ~10.5 wt%, reversible
 - Endohedral metallofullerenes (e.g. Ca₂@C₆₀H₅₂) 6.1 wt%, reversible, ~50 kg H₂/m³ (collaboration with H. Dorn at Virginia Tech).
- APCI designed porous nitrogen-doped graphite intercalation complexes that exhibit practical H₂ adsorption enthalpies (-20 kJ/mol H₂ at 7.4 wt% H₂ loading).
- PSU and NREL developed models that indicated enhanced hydrogen binding occurs with higher B concentration and curvature (nearly 50% increase). The calculations indicate that B prefers defect/kinked sites, and that these sites have higher hydrogen binding energies.
- NREL calculations determined that maximum hydrogen capacity is achieved for optimal metal-metal distances in metal scaffolded systems. Metal clustering issues were resolved and it was determined that metal atoms stabilize heavily doped carbon cages or carbon nanotubes.
- ORNL calculations utilizing charged fullerenes as a model system showed up to 8 wt% hydrogen uptake, indicating the important role of surface charge in hydrogen storage.



Introduction

Significant improvements over currently available hydrogen storage technologies are required if hydrogen is to become a viable energy carrier. The Hydrogen Storage targets presented in DOE's Multi-year Research Development and Demonstration (RD&D) Plan for the Hydrogen, Fuel Cells, and Infrastructure Technologies (HFCIT) Program state the critical needs and goals. At this time, no known storage system can meet the mass, volume, cost, safety, and efficiency requirements for vehicular hydrogen storage systems. Consequently, DOE is investigating solid-state storage options such as metal hydrides, chemical hydrides, and sorbent materials. Nanostructured carbon and other high surface area materials containing carbon, metals, oxygen, and other elements, show tremendous promise for break-through performance in vehicular hydrogen storage. However, the capabilities of these materials remain unclear due to a lack of understanding of both the factors governing their performance and the design principles for synthesizing the materials and constructing the required systems.

HSCoE is developing reversible sorbent materials for hydrogen storage within the U.S. DOE National Hydrogen Storage Program. The center is developing the science base and technology advances required to meet DOE goals for on-board storage of hydrogen by researching a wide range of nanostructured hydrogen adsorbents. A guiding principle in developing the required material is that a continuum of energies exists for hydrogen bound to substrates and molecules. On the weak side of the continuum is non-dissociative physisorption due purely to van der Waals (vdW) forces (4 kJ/mol). On the strong side is the full C-H chemical bond in methane with an energy of ~400 kJ/mol. Between these two limits, with binding energies between 10 and 50 kJ/mol, are: (i) stronger physisorption (due to modification of the key parameters effecting vdW forces), (ii) dihydrogen binding via the formation of complexes that exhibit Kubas-type interactions, and (iii) weak, reversible chemical bonding of mono-atomic hydrogen to strained C-C and other matrices ("spillover"). The DOE goals can be met with sorption-based materials if (i) the energy for hydrogen adsorption can be designed to be in an optimal range (10–50 kJ/mol), and (ii) efficient volumetric arrangement of a sufficient number of suitable binding sites can be achieved with a low-weight material. These goals are difficult to reach in conventional high-surface-area adsorbents that are limited by low physisorption binding energies, heterogeneity of the adsorbent surfaces and adsorption sites, and excessive macroporosity and poor volumetric packing.

Approach

The main goals of the HSCoE is to discover the limits of performance of high surface area adsorbents and to synthesize and test sorbents that will meet the DOE system targets for reversible, on-vehicle hydrogen storage. This involves the design and synthesis of materials that bind large amounts of hydrogen on both a per-weight and a per-volume basis as (i) weakly and reversibly bound atoms and/or (ii) strongly bound molecules. The HSCoE focuses on determining hydrogen binding mechanisms and energies, and the manner in which suitable sites may be organized in space to achieve a high volumetric density using low-weight frameworks. This involves determining the affects of geometry, the introduction of defects, adventitious dopants, catalytic species, as well as elemental substitution. The HSCoE currently investigates a wide range of different lightweight nanomaterials. These include pristine, metal-doped and metal-decorated graphitic materials, CAs, carbon nanohorns, graphite nanofibers, conducting and boron-doped polymers, metal organic frameworks, boron-doped and metal decorated single walled nanotubes, fullerene-metal hybrid materials, and a host of new clusters and nanostructures that are being discovered. In addition to the current materials systems being studied, the HSCoE strives to be nimble and flexible to incorporate promising new ideas, materials, and concepts as they arise.

Results

As previously indicated, the HSCoE is interested in a wide array of materials, the study and development of the hydrogen storage capabilities of these materials, as well as the discovery and development of new, more promising materials. The HSCoE effort is driven by a synergistic interaction between computational modeling, materials synthesis, hydrogen adsorption/desorption characterization, and systems-related engineering concerns. Numerous specific significant results from the FY 2007 HSCoE activities were listed previously. These and others will be discussed in more detail in the partner-specific portions of this report. Here we highlight three notable HSCoE accomplishments.

Hydrogenation as a Room Temperature Storage Mechanism

Last year [1], R.T. Yang's group at the UM demonstrated ~4 wt% reversible hydrogen storage at room temperature and moderate pressures via spillover using a Pt-MOF system. This year, these and other spillover results were independently verified. UM worked closely with NREL and SwRI to provide samples and expertise to reproduce and measure spillover materials. NREL has reproduced the factor of

two increase observed via spillover using Pt-activated carbon materials. Independently, a group at the INER in Taiwan used UM's published material [1] to construct the bridged IRMOF-8 spillover material. Material from INER was provided to SwRI who validated the 4 wt% hydrogen uptake results at room temperature (Figure 1).

In addition to the spillover materials development work, the HSCoE has also developed a detailed understanding of the spillover process. Yang's group at UM and APCI developed detailed mechanistic models to describe the overall processes involved with spillover. In addition, NREL developed a first principles atomistic model for spillover and identified systems in which both the carbon-hydrogen bond strength and the H diffusion barrier are optimal for spillover to take place. Finally, Rice University developed a detailed atomistic model of spillover that accurately addresses the thermodynamics involved. Rice found that specific hydrogen clustering with a localized front enables stable storage and diffusion at the relatively low energies observed in the spillover experiments.

In addition to developing a strong theoretical basis for spillover, additional experimental evidence was obtained by NIST using single-walled nanohorn (SWNH) materials from ORNL, and from hydrogenated materials synthesized at NREL. Evidence for a spillover mechanism in both Pt- and Pd-decorated SWNHs was observed by neutron scattering by monitoring the loss of free H₂ in decorated versus undecorated samples. Also, NREL demonstrated that through proper surface preparation, carbon materials such as activated carbon and SWNTs can be hydrogenated to store ~5 wt% under ambient conditions. Interestingly, the binding energy

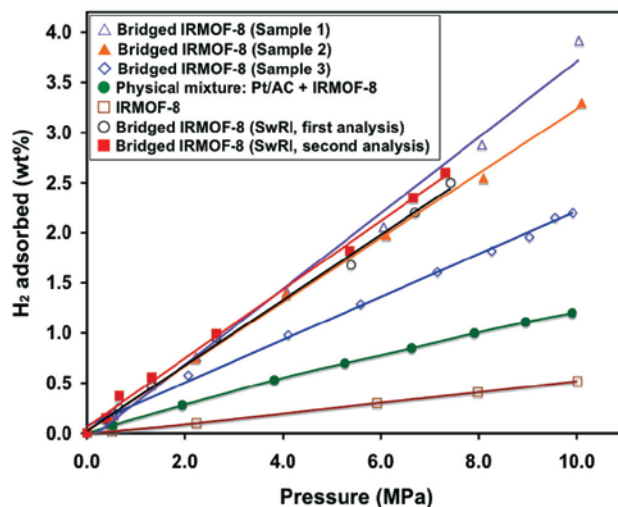


FIGURE 1. Hydrogen storage by bridged IRMOF-8 at 298 K. Comparison of INER-SwRI data and UM data on three samples. The INER-SwRI results used materials made at INER and are from M. A. Miller and R. Page, DOE Annual Merit Review Meeting report, Washington, D.C., May 14–17, 2007, Paper STP 36, "National Testing Laboratory for Solid-State Hydrogen Storage Technologies."

was much lower than would be expected for a relaxed C-H bond. These experimental and computational results demonstrate how the HSCoE is working closely together to accelerate materials development; to demonstrate the viability of spillover for on-vehicle hydrogen storage; and to provide insight to develop improved materials with even better capacities and kinetics.

Enhanced Dihydrogen Sorption

To improve physisorption, both the surface area and binding energy of lightweight materials must be increased in comparison to typical porous carbons. However, as with recent work involving metal organic frameworks, [2] even materials with specific surface areas greater than 5,000 m²/g do not provide substantial improvement for hydrogen sorption at ambient conditions nor even as much adsorption as some carbon materials with nearly half the specific surface area. For example, templated carbon materials [3] with ~3,000 m²/g have recently been project to have over 8 wt% hydrogen uptake at 77 K compared to MOF-177 with nearly 6,000 m²/g that only has ~7 wt% hydrogen storage at 77 K. Thus, while development efforts continue to improve specific surface areas of some materials, the HSCoE is also focusing on developing materials with higher dihydrogen binding energies. Presently, two promising routes are being explored; boron-doping of intrinsic carbon structures and integration of partially coordinated lightweight metals with carbon structures.

As discussed above, NREL and PSU have developed predictive computational models that demonstrate the binding energy enhancements that may be gained from boron-doped carbons. Enhanced concentrations of boron above the presently achieved ~8% level coupled with highly curved surfaces could increase binding energies and permit substantial hydrogen storage capacities at near ambient conditions. The theoretically predicted enhanced dihydrogen binding energies due to boron doping have been indirectly observed in hydrogen capacity measurements and directly observed by nuclear magnetic resonance (NMR) measurements. Using NMR, UNC determined the binding energy of H₂ to boron doped graphitic materials to be ~11 kJ/mol, and provided researchers with feedback to optimize processing. Furthermore, the storage capacity of boron-doped nanoporous carbon (at 5 wt% boron) with specific surface areas between 1,000–1,500 m²/g was ~0.5 wt% at room temperature and 100 bars. This is approximately twice the uptake observed under similar conditions for activated carbon materials with similar surface areas. Thus, since synthetic routes to increase boron doping concentrations exist, further increases in the boron content in combination with appropriate processing to enable access to all sites should provide a

viable approach to hydrogen storage materials that meet the 2010 DOE system targets.

While undoped or doped nanoporous materials may provide a viable hydrogen storage path by themselves, these materials can also be used as lightweight supports to stabilize metals for Kubas-type [4] or hydride binding. In FY 2007, metals were incorporated into porous carbon structures including CA, SWNHs and SWNTs, activated carbon, and fullerenes. Work at LLNL in conjunctions with HRL Laboratories in the Metal Hydride CoE used aerogels as “nanoscaffolds” to provide a structure to stabilize CA/LiBH₄ nanocomposites. This work demonstrated over 8 wt% hydrogen desorption (Figure 2) and a decrease in the desorption temperature along with improved kinetics associated with the smaller hydride particles. In a similar manner, carbon (especially boron-doped) nanostructures can be used to hold partially coordinated lightweight metal atoms and thus create Kubas-type complexes to store dihydrogen. Using guidance from theory, partners in the HSCoE constructed several metal decorated carbon nanoporous and fullerene materials and each demonstrated unique dihydrogen sorption properties. In general, metal distribution and access must be improved to demonstrate the full potential of this hydrogen storage method, but the initial results are promising and indicate that the approach warrants vigorous investigations.

Rational Design of New Hydrogen Storage Materials

In FY 2007, the HSCoE continued to design and identify potential hydrogen storage materials that may be able to meet the DOE targets. In addition to gravimetric and volumetric concerns, emphasis was also placed on identifying materials with viable synthesis pathways that are thermodynamically stable for long durability in the field. Along these lines, the

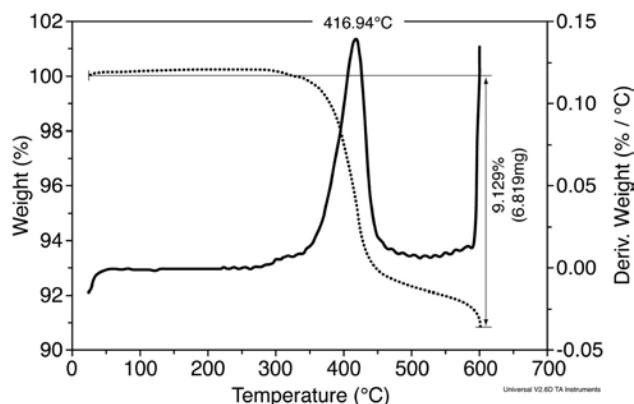


FIGURE 2. Thermal Gravimetric Analysis Performed by HRL Laboratories of the LLNL/HRL CA/LiBH₄ Composite Indicated ~8% H₂ by Weight Desorbed

HSCoE developed first-principle predictive models to define conditions for enhanced binding with boron doping, for optimally placing metals on lightweight supports to achieve maximum hydrogen capacity, and to define stable conditions that prevent clustering and polymerization. These detailed results provide clear guidance for synthetic work. Furthermore, the modeling also identified several new classes of potential hydrogen storage materials. Metalloborane and metallocarborane structures were predicted by NREL to reversibly store over 10 wt% hydrogen at over 50 kg H₂/m³. Also, porous nitrogen-doped graphite intercalation complexes (Figure 3) with practical H₂ adsorption enthalpies (-20 kJ/mol) and ~7.4 wt% uptake were identified by APCI which promise to be more straightforwardly synthesized. Finally, through collaboration with H. Dorn at Virginia Polytechnic Institute and State University, endohedral metallofullerenes (e.g. Ca₂@C₆₀H₅₂ with 6.1 wt% and ~50 kg/m) were identified by NREL as another reversible hydrogen storage material. Since endohedral metallofullerenes are commercially available and have well-defined synthetic routes, tailoring the processing to optimize for hydrogen storage should be straightforward. Thus, the computational efforts in the HSCoE continue to provide key insights for materials discovery, enabling a systematic approach that accelerates hydrogen storage materials development.

Additional details for each of the HSCoE Partners are provided below. This includes a summary of FY 2007 results and FY 2008 Plans for each partner.

Conclusions and Future Directions

- Substantial interactions involving all partners were established to accelerate R&D.

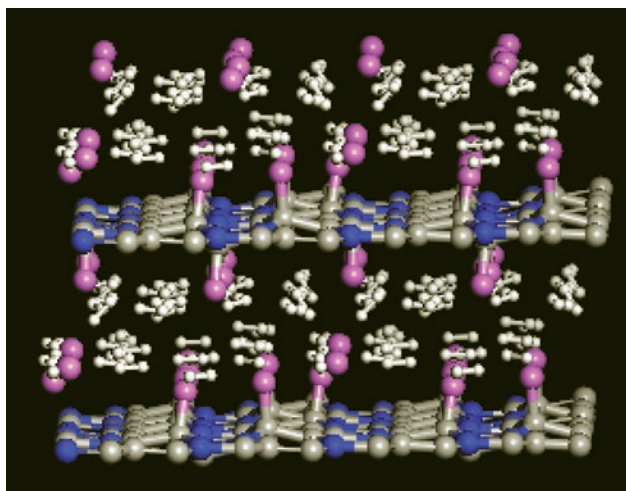


FIGURE 3. APCI Snapshot of the Molecular Dynamics Simulation of 7.4 wt% Hydrogen Adsorption in Porous (C₆N₂)_n2n+ 2nF- (Hydrogen Atoms are White, Fluorine Atoms are Purple, Nitrogen Atoms are Blue, Carbon Atoms are Gray)

- Strong teaming across institutions/topics/expertise.
- Optimized carbon pore structures enhances H₂ uptake, up to 8 wt% possible.
- Partner collaborations have enabled boron doped carbons that bind H₂ at ~10 kJ/mol which may enable a room temperature and moderate pressure H₂ storage system.
- Boron doped carbons will more effectively hold metal atoms, limit aggregation.
- Metal-carbons synthesized and demonstrating unique sorption with higher binding.
- Partner collaborations have led to an improved understanding of spillover and development of additional materials.
- Demonstrated substantial (~5 wt%) irreversible hydrogen capacity of hybrids at standard temperature and pressure.
- Materials discovery efforts have identified several new systems that could meet DOE targets and helped develop synthesis pathways to form others.
- Strong interplay between theory and experiment is identifying weaknesses in approaches, and determining new paths forward.
- Develop and implement synthesis/combinatorial approaches to rapidly identify and test the hydrogen storage performance characteristics of promising materials.
- Optimize nanoporous structures to improve hydrogen storage capacity.
- Perform computations to determine viable synthesis pathways and identify new hydrogen storage materials
- Develop novel synthetic routes to increase boron-doping, create structures with stabilized metal atom dihydrogen complexes, and produce optimized nanoporous structures with access to all desired sorption sites.
- Improve understanding and synthesis of enhance spillover/hydrogenation materials.
- Integrate new projects into center and continue to enhance the efficiency of collaborations to accelerate materials development.

References

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