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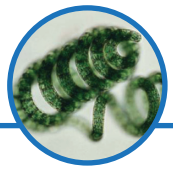
Future prospects for hydrogen storage in designer nanocomposites



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"…we can enhance hydrogen storage capacity, accelerate hydrogen desorption, protect against oxidation and improve cycling capacity."

Anne M Ruminski[1], Rizia Bardhan[1], Alyssa Brand[1] & Jeffrey J Urban[†1]

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Inexorably growing global demands for energy, coupled with the depletion of readily-accessible fossil fuels, urgently necessitates the development of renewable energy sources. To meet these escalating energy needs while still ensuring energy security, many new classes of fuels will be investigated as potential substitutes, including biofuels, synthetic fuels and other alternative energy carriers. These fuels would then be utilized either in traditional internal-combustion engines or in a fuel cell. Fuel cells provide great flexibility for alternative fuels, several distinct types of fuel cell systems exist powered either traditionally (e.g., by oxidation of hydrogen or methanol) [1] or nontraditionally (e.g., by employing microbial communities to oxidize organic molecules) [2]. Indeed, this diversity is evident, as even within hydrogen fuel cells there are a variety of subclasses, including polymer electrolyte membrane fuel cells [3], alkaline fuel cells [4] and phosphoric acid fuel cells [5]. Here, we will discuss the potential of a new hybrid form of matter composed of nanocrystals dispersed in a polymer/carbon matrix to potentially serve as ideal repositories for hydrogen fuels. We will introduce the advantages of materials at the nanoscale and then show how nanocomposites are a potentially practical platform to harness those advantages safely.

Hydrogen has received attention since the 1970s as an alternative energy carrier for internal-combustion engines and fuel cells due to its energy density (142 MJ kg^{-1}), light mass, natural abundance (it is the most abundant element on Earth) and negligible environmental impact as a fuel (the sole combustion product is water). Currently, hydrogen is produced by reforming natural gas, but recent research has focused on a cleaner production of hydrogen through splitting water with sunlight [6]. In addition, studies have shown that select groups of algae can photochemically evolve hydrogen from water [7]. While these results are encouraging, further progress in these fields will be needed to viably produce enough clean hydrogen to meet the rising demands of the energy sector.

Even assuming that hydrogen could be produced cleanly at scale, the lack of efficient hydrogen storage materials would critically limit the widespread adoption of a hydrogen economy. At standard temperature and pressure, hydrogen exists as a gas with very low volumetric density (0.084 g l^{-1}). Current hydrogen-powered vehicles use compressed gas tanks (e.g., Mercedes Benz B-Class F-CELL; 10,000 psi, 30 g l^{-1}) or cryogenic liquid hydrogen (e.g., BMW Hydrogen 7; 70 g l^{-1}) to store sufficient volumetric density of hydrogen for

[1]The Molecular Foundry, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
[†]Author for correspondence: E-mail: jjurban@lbl.gov

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transportation. However, the large mass of the storage container (required for mechanical robustness) and the safety concerns of high pressures involved, are major drawbacks. In addition, liquid hydrogen storage experiences losses due to hydrogen 'boil off' resulting from environmental warming of the tank. Current research in materials science related to hydrogen storage has largely focused on chemical methods of storage. Recent advances in metal hydrides [8], borohydrides [9] and alanates [10] have demonstrated that hydrogen can be reversibly stored in solid-state composite materials via covalent bonding (chemisorption). Alternatively, high-surface-area materials, such as metal–organic frameworks [11], carbon aerogels [12], zeolites [13] and porous polymers [14], make up a second class of materials in which hydrogen is stored through weak interactions on the surface of the material (physisorption). All of these chemical approaches have demonstrated safer and more compact hydrogen storage with higher volumetric and gravimetric density than conventional high-pressure tanks.

In addition to safety and capacity, viable storage materials need to be affordable, have acceptable thermodynamics and have fast kinetics. Recent research in thin films [15], clusters [16] and nanocrystals [17] have demonstrated that enhanced kinetics is achievable by size reduction of the crystalline domains of the storage medium to the nanoscale. These observed kinetic improvements were not unique to a particular chemical system, but were recorded for a variety of materials, signifying that nanoscaling of materials to fundamental gaseous mean free paths is a key route for improving kinetics in hydrogen storage systems.

The large storage capacity of metal hydrides (e.g., 7.6 weight% as MgH_2) renders them appealing targets for stable storage media. However, high-bond formation enthalpies, slow uptake and release kinetics, and poor oxidative stability remain major barriers to the implementation of metal hydrides for practical use. Fortunately, recent studies have shown that nanostructuring of magnesium can increase both absorption and desorption kinetics. Theoretical calculations [16] and metal-catalyzed thin-film studies [15] attribute this enhancement to the decrease in diffusion path lengths for hydrogen and decrease in thickness of the poorly permeable hydride layer that forms during absorption. Moreover, while bulk magnesium requires temperatures of approximately 400°C for several hours for hydrogenation and dehydrogenation to proceed, magnesium nanowires (diameter of 30–50 nm; length ~several micrometers) exhibit full hydrogenation within 30 min at 300°C [8]. Activation energies for hydriding/dehydriding in these wires were measured to be 33.5/38.8 kJ mol^{-1} H_2, almost 100 kJ mol^{-1} H_2 lower than that of bulk magnesium hydride at 120–142 kJ mol^{-1} H_2. Thus, practical kinetic rate enhancements can be achieved without sacrificing storage density.

Although metal hydrides at the nanoscale show enhanced kinetics, the decrease in material size and resultant increase in surface area also makes them much more susceptible to oxidation. Nanoscale magnesium oxidizes instantaneously when exposed to even minuscule concentrations of oxygen and water, resulting in an oxide layer that greatly inhibits hydrogen penetration. Formation of polymer nanocomposites offers one approach to surmounting these challenges while retaining the appealing features of the intrinsic nanoscale metal hydrides. Our group, for example, has encapsulated magnesium nanoparticles (5 nm in diameter) in a gas-selective polymer, poly(methyl methacrylate) (PMMA) [18]. PMMA holds a H_2/O_2 permeability ratio of 42.9 at 35°C. Magnesium nanocrystal–PMMA composites are remarkably resistant to oxidation; even after 2 weeks of air exposure, the composite showed no trace oxide peaks in atomic resolution transmission electron microscope diffractograms. These nanocomposites also display enhanced kinetics over bulk magnesium, recording hydriding/dehydriding activation energies of 25/79 kJ mol^{-1}, respectively. Moreover, an experimental volumetric hydrogen capacity of the composites was calculated at 55 g l^{-1}, far exceeding the volumetric capacity of compressed (30 g l^{-1}) hydrogen gas. Current efforts aim to increase the number density of magnesium nanocrystals safely embedded in the composite, which should further increase the storage capacity.

In addition to binary metal hydrides, alanates are another class of materials that chemically store hydrogen. The alanates, similarly to magnesium, are lightweight and high hydrogen storage capacity materials (e.g., 10.5 and 7.4 weight% for $LiAlH_4$ and $NaAlH_4$, respectively). While sodium alanate ($NaAlH_4$) possesses favorable thermodynamic properties, high activation energies of bulk $NaAlH_4$ restrain hydrogen release and uptake, limiting its practical use. Recent developments have lowered these activation energies by preparing composites of nanoscale sodium alanate supported on carbon nanofibers [19]. Nanocomposites containing particles with a diameter ranging between 2–10 nm exhibited an activation energy for H_2 desorption of 58 kJ mol^{-1}, considerably lower than bulk $NaAlH_4$ (120 kJ mol^{-1}). Similarly, the desorption activation energy of $LiBH_4$ has been reduced from the bulk value through incorporation in a nanoporous carbon aerogel host [20]. The carbon aerogel behaves as a scaffold, restricting the particle size of melt-infiltrated $LiBH_4$. Bulk $LiBH_4$ has an activation energy of 146 kJ mol^{-1},

whereas the activation energy of $LiBH_4$/carbon aerogel (13 nm diameter pores) nanocomposites was lowered to 103 kJ mol^{-1}. The novel composite materials detailed above containing nanoscale borohydrides, alanates and metal hydrides all exhibited impressive kinetic enhancements, rendering nanocomposites as promising hydrogen storage materials that warrant additional focus and development.

As we have described, many improvements in hydrogen storage materials have been realized through nanostructuring and formation of composite materials; however, major scientific breakthroughs are still necessary for transitioning hydrogen storage materials from bench-scale to commercialization. A successful material for hydrogen storage in a vehicle would have enough storage capability to allow a driving range of greater than 300 miles (500 km) without interfering with passenger or luggage compartment spaces or adding excessive weight to the vehicle. Hence, improving gravimetric and volumetric densities of the material are key to on-board vehicular applications. In addition, rapid hydrogen uptake when refueling and reasonable operating temperatures will be crucial for the material's success. The US Department of Energy has set target minimum/maximum delivery temperatures for 2015 of -40 to 85°C. Accessing this temperature range remains problematic for most hydrogen storage materials currently under study, including materials at the nanoscale. For example, the magnesium nanowires, magnesium nanocrystal–PMMA composites and the nanoconfined $LiBH_4$ composites detailed above had hydrogen delivery temperatures of 200–300°C. However, the nanoscale $NaAlH_4$ did have an acceptable desorption temperature of 70°C, which is encouraging for future developments in chemical nanocomposites.

Through the combined efforts of the entire scientific community in both academia and industry, we are gaining a better understanding of how hydrogen interacts with materials. The exciting results of the past decade have shown that through manipulation of the material composition (C, Mg, Li, Pd and Ni), shape, size and environmental matrix, we can enhance hydrogen storage capacity, accelerate hydrogen desorption, protect against oxidation and improve cycling capacity. The improvements made to date are promising that with future work the scientific community will reach the targets set by the Department of Energy, continuing the momentum towards a hydrogen-driven economy.

Financial & competing interests disclosure

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