

HYDROGEN STORAGE USING CARBON-BASED MATERIALS

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A major step towards implementing an overall hydrogen-based energy economy is to develop fuel-cell-powered vehicles for the transportation sector. The transportation sector is targeted for early deployment because the U.S. currently imports approximately 50% of the petroleum we consume, and this value is projected to rise significantly in the future. Also, carbon sequestration strategies for ameliorating potential problems associated with global warming are much more difficult to implement with mobile sources than with stationary ones. The development of hydrogen-powered vehicles could produce overall reductions in CO₂ emissions even if the hydrogen fuel was generated from fossil fuels by, e.g., steam reforming of natural gas at a stationary production facility. Such vehicles could be seamlessly integrated with renewable energy-based methods for hydrogen production as they become available in the future.

If the transportation sector of the economy is to move from fossil fuels to hydrogen, vehicular storage systems must be low-cost, high-density, safe, and efficient. Unfortunately, no such systems are currently available. The challenge to develop viable hydrogen storage materials is somewhat daunting when one considers that an effective hydrogen-storage sorbent must possess; (i) a binding energy that permits strong enough but yet reversible immobilization of H or H₂, (ii) a sufficient density in space of the energetically-correct binding sites, and (iii) a low-weight skeletal framework. Additional constraints include the need for energy efficient charge and discharge. The U.S. DOE's Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program has 2010 *system* storage targets of 6 wt% and 45 gH₂/L.

Possible approaches to vehicular hydrogen storage include: (i) physical storage via compression or liquefaction, (ii) reversible conventional metal hydrides (e.g. MgNi₃), (iii) complex metal hydrides (e.g. NaAlH₄), (iv) chemical storage in irreversible hydrogen carriers that must be regenerated off-board (e.g. NaBH₄), and (v) reversible adsorption on nanostructured high-surface area materials such as metal-organic frameworks (MOFs) and carbon-based materials. Although each storage method possesses some desirable attributes, no approach satisfies all of the efficiency, size, weight, cost, and safety requirements for transportation vehicles (see: <http://www.eere.energy.gov/hydrogenandfuelcells/mypp/>).

High surface area carbon materials have been studied for possible use in hydrogen storage applications for nearly four decades. These efforts have been motivated by the idea that hydrogen molecules might be localized on a solid support in high density via attractive interactions, such as van der Waals forces. During the first three decades of effort researchers were limited to studies on materials prepared by thermochemical processes using mineralogical or biological precursors. These carbon materials typically

exhibited substantial polydispersity in chemical and physical structure and produced only weak interactions with hydrogen. Thus, useful amounts of hydrogen (> 5 wt%) could only be localized on the substrate by adsorption at cryogenic temperatures and relatively high pressures. In recent years the availability of nanostructured carbon materials, such as single- and multi-walled carbon nanotubes, graphite nanofibers, and metal-decorated and doped versions of these has reinvigorated hydrogen storage studies of carbon-based hydrogen sorbents. Since the first report on hydrogen storage in single-wall carbon nanotubes in 1997, hundreds of theoretical and experimental investigations have been performed to determine the hydrogen storage properties of nanostructured carbons. Unfortunately, the recent scientific literature is full of inconsistent findings with reported capacity data at room temperature ranging from 0 to 60 wt%. Recent work in our laboratory indicates that up to 8 wt.% hydrogen may be stored on SWNTs at room temperature when catalytic metallic species are purposefully introduced. Other reports indicate that room temperature storage capacities using SWNTs are negligible (0.1 wt%).

Within the body of published work are rigorous, detailed efforts that indicate that properly designed carbon-materials may offer a break-through in hydrogen storage performance. However, the published data is confusing because nominally similar experiments from different labs yield inconsistent results. Additionally, there is considerable debate over the nature of the physical and chemical mechanisms that could yield stable, reversibly bound hydrogen at room temperatures. The scatter in the results is probably due to the different ways in which samples are synthesized and activated, the quality of the samples, the concentration of the desired carbon nanostructures within the samples, errors brought about by leaks or impure gasses, and variations in sample handling and testing protocols. For example, it is interesting to note that a vast majority of the reported data has been obtained under conditions where the surfaces of the nanostructured carbon adsorbents were already populated by species due to adsorption from, or reaction with, laboratory air species. In these studies, a high temperature degas in a clean vacuum, a process that is necessary to produce a clean adsorbent surface, was typically not performed. Thus, the true hydrogen adsorption properties of the nanoscale carbons were not actually being measured.

In this talk, we will examine the literature and focus on several key findings that clearly illustrate the promise of engineered carbon-based nanostructures for hydrogen storage. In particular, we will discuss research avenues that may lead to the development of materials capable of reproducibly binding hydrogen at the DOE FY2010 volumetric and gravimetric density goals (6 wt.% and 45g H₂/L) with energies between ~20 and 40 kJ/mol. We will discuss the experimental and theoretical evidence for both (i) the dissociative adsorption on carbon that is weaker than the typical C-H bond formation, and (ii) the non-dissociative adsorption that is stronger than pure physisorption. In the first case we will consider reversible hydrogen spillover, while in the second we consider molecular adsorption on materials that have undergone structural and/or chemical modifications.