Objectives

- Demonstrate high-capacity hydrogen storage in high surface area carbon aerogels (CAs).
- Develop carbon-based sorbent materials that can store hydrogen at ambient temperature and reasonable operating pressures.
- Fabricate porous carbons as scaffolds for complex hydride systems to improve the kinetic performance of the hydride.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- System Weight and Volume
- System Cost
- Efficiency
- Lack of Understanding of Hydrogen Physisorption and Chemisorption
- Reproducibility of Performance

Technical Targets

This effort is focused on the design of new nanostructured carbon-based materials that meet the former DOE 2010 targets for on-board vehicle hydrogen storage of 6 percent hydrogen by weight and 45 grams of hydrogen per liter.

Accomplishments

- New monolithic carbon aerogels derived from sugars (i.e. sucrose, glucose) have been synthesized for use as spillover substrates. These materials possess surface areas up to 600 m²/g and can readily be doped with hydrogen dissociation catalysts, such as platinum or nickel.
- Novel CA-carbon nanotube (CNT) scaffolds have been prepared through catalyzed chemical vapor deposition (CVD) growth of CNTs on the inner pore surfaces of high surface area CA substrates. These substrates promote intimate contact between the surfaces of the CNTs and the incorporated complex hydride, thus influencing the kinetics of hydrogen exchange in the hydride.
- LiBH₄ nanocomposites prepared with the CA-CNT scaffolds showed significant decreases in the temperature of hydrogen desorption relative to that of bulk LiBH₄. These scaffolds also appear to outperform CA scaffolds prepared without CNT. Work performed in collaboration with Metal Hydride Center of Excellence (MHCoE) members at HRL Laboratories.

Introduction

Porous carbon materials are promising candidates for hydrogen sorption due their lightweight frameworks and high accessible surface areas. The low hydrogen binding energies, however, that are typical of carbonaceous sorbents (≈6 kJ/mol H₂), require that cryogenic temperatures (77 K) be utilized for storage of hydrogen in these materials. In general, the amount of surface excess hydrogen adsorbed on porous carbons at 77 K and ~3.5 MPa varies linearly with Brunauer-Emmett-Teller surface area; gravimetric uptake is ~1 wt% H₂ per 500 m²/g of surface area. Our overall goal in this effort is the design of novel carbon nanostructures that exhibit enhanced binding energies for hydrogen and thus allows for reversible hydrogen storage at ambient temperature and reasonable operating pressures.

Approach

CAs are a unique class of porous materials that possess a number of desirable structural features for the storage of hydrogen, including high surface areas (over 3,000 m²/g), continuous and tunable porosities, and variable densities. In addition, the flexibility associated with CA synthesis allows for the incorporation of
IV.C Hydrogen Storage / Hydrogen Sorption CoE

Results

Design of New Spillover Receptors Derived from Carbon Aerogels

Over the last review period, our work as part of the Hydrogen Sorption Center of Excellence (HSCoE) has been focused on the design of novel spillover receptor materials that can potentially improve both capacity and uptake kinetics in spillover materials. Specifically, we have synthesized novel CAs derived from sugars as spillover receptors. This approach builds on the concept developed by Yang et al. of using partially carbonized sugars as “bridges” to facilitate hydrogen diffusion from the catalyst to the receptor. Our material, however, is comprised entirely of “bridge” material and, therefore, these materials should provide sufficiently favorable surfaces for hydrogen spillover. The carbonized sugar aerogels are prepared through the sol-gel polymerization of simple sugars, such as glucose or sucrose, affording highly cross-linked sugar gels. These gels are then supercritically dried and subsequently pyrolyzed under an inert atmosphere to afford the sugar-derived carbon aerogels. These materials are monolithic and possess surface areas up to 600 m²/g. In addition, these porous carbon structures can be readily doped with hydrogen dissociation catalysts, such as platinum, ruthenium or nickel, by either solution- or vapor-phase techniques. Room temperature hydrogen uptake in the metal-loaded sugar-derived CAs has not yet been evaluated within the HSCoE.

Carbon Aerogel as Scaffolds for Complex Hydrides

For our work with the MHCoE, we fabricated a new class of CA scaffolds that contain dispersions of CNTs within the scaffold framework. Incorporation of CNTs into the scaffold has the potential to not only improve the thermal conductivity of the scaffold, but may also affect the kinetics of dehydrogenation for
certain metal hydrides. Recent work by other groups have indicated that the interaction of the hydride with an electronegative surface, such as that of a carbon fullerene or nanotube, can disrupt the bonding structure of the hydride and, as a result, provide lower energy pathways for hydrogen exchange. These novel CA-CNT scaffolds (Figure 1) were been prepared through the growth of CNTs by CVD on the inner porosity of high surface area carbon aerogel substrates. Because the CNTs populate the surfaces of the CA support, these scaffolds promote intimate contact between the surfaces of the CNTs and the incorporated metal hydride. To evaluate the influence of the CNTs on the kinetics of hydrogen exchange in LiBH$_4$, the hydride was incorporated into the free pore volume of these scaffolds using melt infusion techniques and the temperature of dehydrogenation was determined using thermogravimetric analysis. As shown in Figure 2, LiBH$_4$ nanocomposites prepared with the CA-CNT scaffolds showed significant decreases in the temperature of hydrogen desorption relative to that for bulk LiBH$_4$ and also out-perform earlier generation CA scaffolds prepared without CNT. This approach to scaffold design appears promising and we expect further improvements in performance as the structure of these composite scaffolds are optimized.

Conclusions and Future Directions

While this project finished at the end of this review period, we believe there are a number of aspects of this work that warrant future investigation based on the promising results from Fiscal Year (FY) 2010, including:

- Evaluation of room temperature hydrogen uptake (both capacity and kinetics) in the metal-loaded sugar-derived CAs. These results should provide guidance for further optimization of the surface chemistry and texture of the spillover receptors.
- Further investigation of the influence of CNTs and other graphitic nanostructures on the kinetics of hydrogen exchange in complex hydride systems. Initial results for our CA-CNT composites indicate improved kinetic performance of LiBH$_4$ in these scaffolds.
- Incorporation of other destabilizing agents and catalysts, such as Mg, Ni or Ti, into these CA-CNT scaffolds to facilitate the hydriding and dehydriding processes.

FY 2010 Publications/Presentations


