

STANDARDIZED TESTING PROGRAM FOR EMERGENT CHEMICAL HYDRIDE AND CARBON STORAGE TECHNOLOGIES

Richard A. Page
and
Michael A. Miller

Southwest Research Institute™
6220 Culebra Road
San Antonio, TX 78238

Abstract

Considerable effort and expense are being expended in projects to develop variable chemical hydride/carbon hydrogen storage systems. The development of a standardized protocol and testing system for assessing the performance of these materials and systems will allow both DOE and the R&D organizations to assess the potential performance of the wide array of materials and systems and focus their efforts on those that show the most promise. The presence of performance and safety standards will also speed implementation once viable storage systems are developed. An innovative approach that addresses both performance and safety has been developed. The standardized testing facility that is being developed in this project will have the ability to determine the performance of the storage materials and evaluate the performance and safety of complete storage systems.

Introduction

The steady growth in the development and proliferation of economically viable fuel-cell power-generation systems for vehicular and stationary applications has led to an urgent need for accelerated development of hydrogen storage systems. In vehicular applications, hydrogen storage and distribution presents the greatest challenge in creating the hydrogen fuel infrastructure that is needed to meet the requirements of vehicle designs based upon fuel-cell power generation systems. The choices of viable hydrogen storage systems at this time are limited to compressed hydrogen gas (CH_2), cryogenic liquid hydrogen (LH_2), chemical hydride adsorption, and carbon hydrogen adsorption. While each of these enabling storage technologies have specific advantages and disadvantages, chemical hydride and carbon adsorption storage systems have been demonstrated to be the most viable in terms of storage capacity, refueling time, economic factors and, most importantly, safety.

Interest in metallic hydrides increased after Bogdanovic and Schwickardi identified a new class of alkali metal hydride that, when doped with a catalyst such as TiCl , significantly enhances the kinetics of molecular hydrogen desorption and renders the dehydrogenating process reversible under moderate conditions. These new catalytically enhanced hydride materials, based on the

aluminum hydride complex (AlH_4^-) and any alkali metal (Na, Li, Mg, Zr), are light-weight, store upwards of 5% H_2 by mass, and release it below 200°C , thereby overcoming the limitations of metallic (interstitial) hydrides.

Nearly concurrent with discovery of these new forms of metal hydride materials, remarkable progress was made in the bulk fabrication of carbon fullerene and carbon nanotube materials to the extent that the commercial viability of these materials as hydrogen storage substrates has been reexamined. Theoretical estimates, and many exaggerated or questionable claims, of the intrinsic loading capacity of carbon nanotubes for molecular hydrogen suggested early in their discovery that structurally consistent forms of these materials could be ideal substrates for hydrogen storage. After much speculation, and with the availability of tangible experimental evidence, there is now a general consensus among the scientific community that purified structural forms of single-wall carbon nanotubes can achieve adsorption capacities for hydrogen in the range of 3.5-4.5 weight % under ambient conditions in several minutes.

Both the most advanced metal hydride and carbon nanotube systems to date fall slightly short of the DOE energy density goals of 6.5 weight % for vehicular hydrogen storage. But significant technological advancements on chemical variations of metal hydride and carbon materials are expected to meet or surpass that goal within the present decade. Moreover, the market prospects for fuel-cell-based energy conversion systems are recognized to have tremendous opportunities in the near future. The requirement that commercially viable hydrogen storage systems must be available to realize that market has stimulated world-wide interest among the scientific and engineering community to develop new materials and storage technologies.

Program Need

The realization that chemical hydride and carbon storage systems will most efficiently meet the storage capacity and safety requirements of a hydrogen-based infrastructure has led to significant interest and monetary investment to accelerate the development of complete hydrogen adsorption storage systems. However, there are no standard guidelines, dedicated facilities, nor certification programs specifically aimed at testing and assessing the performance, safety and life cycle of these emergent systems. The development of a standardized protocol and testing system for assessing the performance of these materials and systems would allow both DOE and the R&D organizations to assess the potential performance of the wide array of materials and systems and focus their efforts on those that show the most promise.

Technical Approach Overview

In anticipation of the availability of many new materials and technologies for hydrogen storage, the purpose of the present effort is to develop an evaluation facility with established evaluation protocols and standards for the testing and assessment of these emergent chemical hydride and carbon storage materials or systems. Upon thorough validation of the experimental apparatuses and associated protocols, the testing facility and the technical staff that supports it will be available as the focal testing center to any prospective innovator of chemical hydride or carbon hydrogen storage materials or system. In this capacity, the principal objective of the standardized testing program is to certify the performance characteristics of candidate materials and systems under standardized protocols, and to facilitate their acceptance by integrators and developers of hydrogen storage subsystems for vehicular, stationary, or portable applications.

The protocols that are complementary to the testing facility will allow developers and producers (clients) of candidate hydrogen storage materials to determine, in advance of their product

evaluation, the extent to which their material or system technology will need to be tested, and what would be entailed in evaluating the performance characteristics of their product to determine, if so desired, the acceptability of that technology. Furthermore, all relevant aspects of the emerging technology related to material composition and product preparation will be subject to evaluation and certification to the extent permissible by the client in avoidance of trade secrets.

Although the final form of the test protocols and test equipment are still being defined, it is anticipated that the facility will be centered around hydrogen sorption/desorption measurements of smaller quantities of storage media. An ability to test complete storage systems will also be included. Testing of complete systems is required in order to validate the system performance models that are being developed as part of the project. An overview of the overall project plan is provided in Figure 1.

The performance characteristics of candidate materials will be determined through a comprehensive materials characterization and systems testing approach. This approach will encompass the elements described below.

Certification of Chemical Composition and Crystallographic Properties

Materials selected for evaluation will be analyzed to determine or verify their elemental composition and crystallographic properties using appropriate analytical capabilities: atomic adsorption spectroscopy (AAS), X-ray fluorescence (XRF), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and powder X-ray diffraction.

Evaluation And Certification Of Performance Parameters

The intrinsic thermodynamic characteristics of candidate storage materials, where existing data is not available, will be evaluated by modulated differential scanning calorimetry (MDSC). Data of this sort that has already been generated by others will be used to the extent that it is relevant to the specific goals of the present study. The intrinsic thermodynamic characteristics that will be derived from the MDSC analysis include the following:

- Determination of first-and second order phase transitions
- Heat of transition
- Transition temperature
- Non-reversible transitions (such as in decomposition)
- Decomposition temperature
- Decomposition exotherm
- Crystalline versus amorphous compositions

Once the intrinsic thermodynamic characteristics are firmly established, the storage materials will be subjected to the performance assessment test protocols. The performance parameters and conditions that will be derived from the testing regime are as follows.

- Specific energy contained in storage system (LHV H₂ per mass of total system)
- Sorption/desorption cycle life
- Resistance to exogenous contaminants
- Average refueling time
- Most favorable thermal-cycle condition

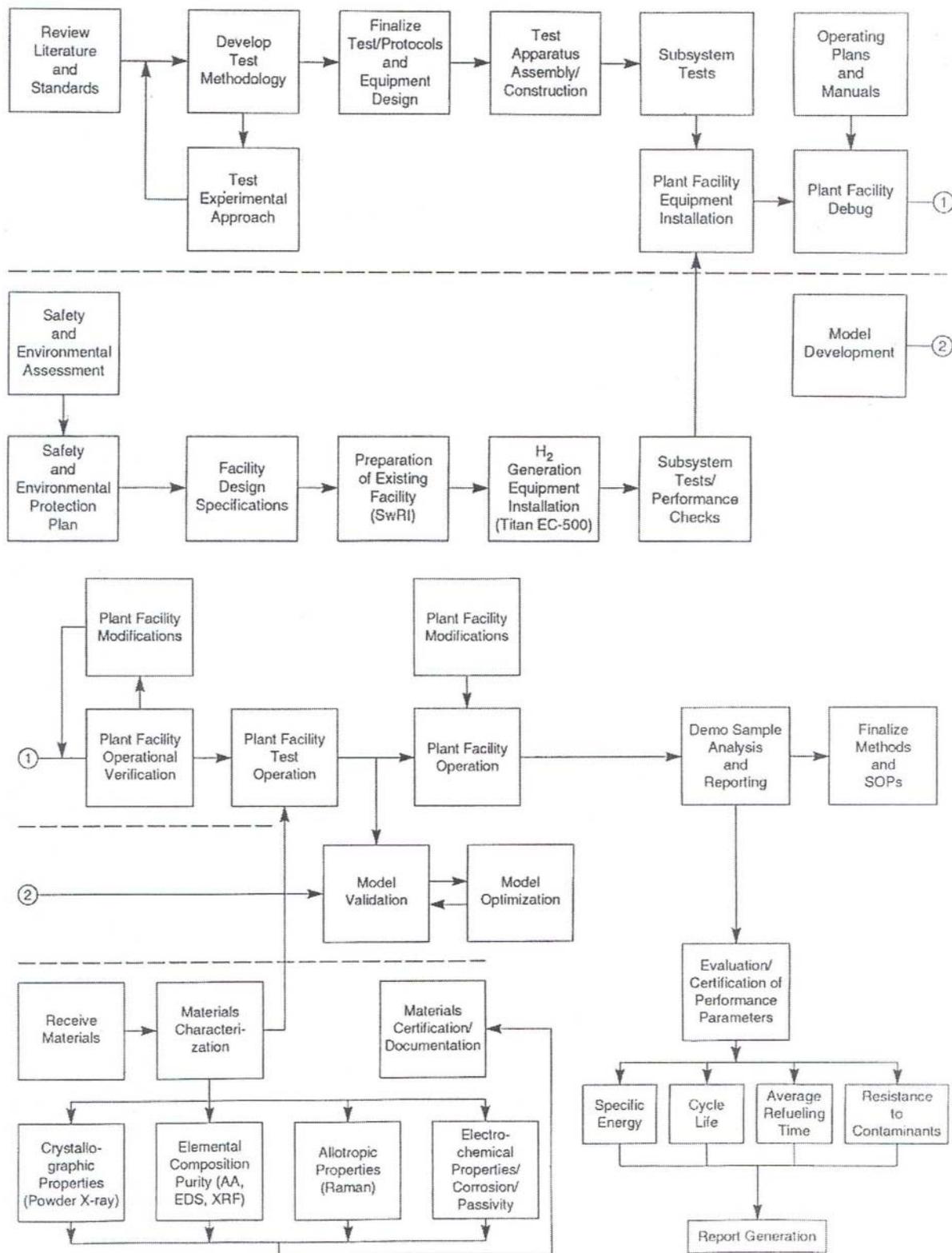


Figure 1. Program Plan Sequence

- Impact resistance (only applicable to complete hydrogen storage container technologies)
- Vibration resistance (only applicable to complete hydrogen storage container technologies)
- Fire resistance (only applicable to complete hydrogen storage container technologies)

Current Status

At the time of this report, the project had been underway for two months. During that period a comprehensive review of current accepted practices was initiated. Discussions with potential suppliers of test equipment were also initiated.

Future Effort

Based on the results of the review of current accepted practices, a report detailing the proposed test protocols will be submitted to DOE. Following DOE approval of the test protocols, design and construction of the test facility will commence.

References

1. Bogdanovic, B. and Schwickardi, M., (1997), J. Alloys and Compounds, 1-9:253.
2. Dillion, A.C. et al., (1999), Proceedings of the 1999 U. S. DOE Hydrogen Program Review, NREL/CP-570-26938.