

## IV.F.7 Safety Properties of Hydrogen Storage Materials

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### Objectives

- Quantify chemical processes and hazards associated with the contamination of hydrogen storage materials.
- Quantify safety and performance degradation effects during low-level cyclic contamination of hydrogen storage materials.
- Predict processes during accident scenarios of systems containing hydrogen storage materials.
- Identify and demonstrate ex-situ and *in situ* hazard mitigation strategies.

### Technical Barriers

This project primarily addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

- (D) Durability/Operability
- (F) Codes and Standards
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

### Technical Targets

A successful effort in quantifying the safety properties of hydrogen storage materials will enable the safe design, production, handling, operation, and disposal of automotive hydrogen storage systems. This effort explicitly addresses the following MYRDDP technical targets:

- **Safety and toxicity:** The DOE performance goals for hydrogen storage systems (2006 MYRDDP) are driven by industry and customer requirements. The targets for safety and toxicity are less tangible than hydrogen sorption and capacity; however, the health and well-being of the vehicle worker/owner/consumer is of the highest significance. Quantifying the hazards associated with contamination scenarios allows for the design of safe hydrogen storage systems based on reactive, energy-dense materials.
- **Cycle life (1/4 tank to full) and cycle life variation:** Each fill cycle represents an opportunity to contaminate the bed. Considering 500 to 1,500 refueling cycles during the lifetime of the storage tank, significant opportunity exists for performance degradation due to contamination. By quantifying the effect of periodic low-level contamination during the duty cycle, we will guide safe system design, appropriate refueling technology, and hydrogen purity codes.

### Approach

We will enable the design and implementation of safe hydride-based hydrogen storage systems by leveraging expertise in chemical processes and experimental kinetics measurement and experimentally-validated computational analysis. The approach is organized into four highly-coupled efforts:

- A. Identify chemical processes and hazards associated with hydrogen storage material exposure to air, water, and other relevant contaminants. Established capabilities including simultaneous thermo-gravimetric modulated-beam mass spectrometry, surface chemical imaging with precision mass analysis, and X-ray diffractometry will be utilized to identify and/or quantify the products, pathways, and rates of reaction occurring between the hydrogen storage material and potential contaminants. Application specific testing will be identified during this effort based on the chemical processes identified. For example, if a meta-stable state is identified, sensitivity to handling will be investigated further to establish handling protocols. Similarly, toxicology data will be reviewed for identified reaction products resulting from contamination events. The experimental data gathered during this task will be used to validate science-based chemical reaction models that will allow the prediction of reaction rates under various conditions of temperature, pressure, and chemical composition. The contamination reactions will be described by a mathematically complex system. It is likely (as

the experiments will verify) that the solid-phase reactants and products have well-defined chemical compositions, indicating that the reactions must be heterogeneous rather than homogeneous, i.e., they can take place only at the surfaces of the solid phases. This implies that expressions must first be formulated for the surface reaction rates, which can depend only on the concentrations of gas-phase species (as well as temperature). Surface area per unit volume then becomes a crucial variable, and a geometric model of the particle bed will be needed to relate these varying surface areas to the overall (volume-averaged) concentrations of the solid-phase species. The combination of the surface reaction and geometric models will give the desired final expressions for the volumetric reaction rates entirely in terms of macroscopic concentrations. It may also be necessary to account for the transport of gas-phase species through a growing solid product layer. We will rely on experimental observations to identify reaction products and stoichiometries, to give an indication of the particle morphologies, and to provide quantitative data on reaction rates. This reaction-rate data will be used in a parameter-estimation procedure to infer the temperature-dependent intrinsic rate constants for the surface reactions, since these cannot realistically be predicted from first principles. The model will be validated by the degree of success of the optimized parameters in allowing the model to fit all of the available data.

- B. Quantify safety and hydrogen sorption performance degradation as a function of exposure to contamination (especially air and water). The goals for loss of useable capacity as outlined in the MYRDDP will be attained by understanding the effects of low level oxygen and water exposure on hydrogen sorption. Accelerated aging experiments will be designed and performed to simulate low-level contamination as may be experienced during the operational lifetime of the storage system. End-of-life handling hazards will be identified and hydrogen sorption performance will be experimentally quantified on a volumetric apparatus (Sieverts) for different levels of contaminant exposure. Validated models will be built and used to describe the overall durability of the storage material as a function of contamination history and characteristics. Effect on hydrogen capacity and sorption rate will be quantified as a function of oxidation level and hydrogen cycling utilizing the chemical models developed in Task A described above.
- C. Predict chemical processes during accident scenarios using fully coupled, dynamic and validated models of high-level air and water exposure processes to provide insight for the design of integrated safety systems and accident response.

The system level effort will extend the local reaction models developed in Task A to larger-scale system contamination reactions. Coupled chemical, heat, and mass transfer models will be developed using (mostly) existing finite element codes. These multi-physics problems are unsteady, three-dimensional and are consequently very large and difficult to solve. Our codes allow for the analysis of large problems by using parallel numerical architecture along with large-scale multi-processor computers. The models will be validated experimentally using custom test hardware fabricated with appropriate vessel geometries and operating conditions and containing storage materials with appropriate morphologies. Operational pressures and temperatures will be considered carefully since they are expected to exert a large effect on mass diffusion and reaction rate. Example test hardware will likely consist of a characteristic thin wall pressure vessel that is realistically exposed to ambient air. System geometry is expected to exert influence on the reaction advancement through the bed; thus only relevant geometries under consideration within the DOE Hydrogen Storage Program will be investigated.

- D. Identify hazard mitigation strategies for handling and disposal of contaminated hydride materials. Methods will be identified and demonstrated to convert hazardous oxidation products of hydride storage materials into stable compounds for safe handling and disposal. Developed methods will be applicable to a variety of solid hydride storage materials that are under investigation within the DOE Hydrogen Program. Hazard mitigation techniques must apply to hydrogen storage beds that have unknown contamination histories or have been compromised by atmospheric gases. Caustic oxidation products must be neutralized and metastable energetic products, such as peroxides or superoxides, must be deactivated. It may also be necessary to passivate the bed against subsequent oxidation reactions depending on the prospects for handling or access to the material. An example of a hazard mitigation approach is the use of gaseous neutralizing agents to convert reaction products to stable forms. Gaseous agents facilitate *in situ* treatment because of the ability to access all of the bed material without the need to disturb or remove it. We will determine rates of mitigation reactions for the spectrum of oxidation products, derived from a broad range of hydride materials. We will emphasize carbon dioxide as the neutralizing agent, although other acidic gases will be investigated. Rates will be determined quantitatively so that results can be extrapolated to potentially diffusion-controlled conditions that may apply with packed beds of hydride materials. This study will also

entail an assessment of methods to determine, 1) the chemical state of the bed materials with regard to oxidation products and techniques, 2) the progress of prospective mitigation treatments, and 3) the end-state success of the neutralizing process. The developed hazard mitigation techniques can eventually be utilized to implement material handling protocols and *in situ* engineering controls.

This effort does not target a specific material or storage system design but rather focuses on developing capabilities to quantify the safety properties of high energy density hydrogen storage materials in general.

The work plan is designed to conform to the progression of new materials and systems development within the DOE Hydrogen Storage Program. The project is divided into two phases; during Phase I, generalized analysis methods and procedures will be developed and validated based on current state-of-the-art materials. Exclusive capabilities that cannot be extended to new materials will not be actively pursued. During Phase II, new materials will be identified and modifications, additions, and/or deletions to the capability will be implemented. Ultimately, the methods, procedures, and validated models will allow for the design and implementation of hazard mitigating features applicable to full-scale automotive systems.