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This document appeared in

Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 4: Storage Systems / Policy Perspectives, Initiatives and Co-operations
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-4
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-654-5

Optimization of Hydrogen Uptake and Release in Automotive-scale Metal Hydride Systems

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Abstract
Metal hydride systems provide a technology pathway for high energy density hydrogen storage systems for a variety of transportation, APU, and man-portable power applications. Since metal hydride based systems include highly coupled heat transfer, mass transfer, and chemical kinetics, many opportunities exist for bottlenecks in the engineered system. For example, large variations in pressure and temperature can develop in the hydride material during refueling processes that can effectively starve parts of the system of hydrogen while other parts become over heated and cease to absorb hydrogen. In order to accurately resolve the local reaction environments present, the transport of gas through the bed must be understood. Towards this end, we have developed mass transport, heat transport, and chemical kinetics models that allow us to accurately predict hydrogen refueling and release processes for metal hydride based hydrogen storage systems. We have validated these models by comparing predicted results to experimental bulk hydrogen uptake/release rates and the associated thermal response of a 1.7kg sodium alanate system. Numerical experiments using these validated models resulted in a subset of design concepts that allow for optimized hydrogen uptake and release for transportation applications.

1 Metal Hydride Based Systems

Sodium aluminum tetra-hydride ($NaAlH_4$), a complex hydride historically used as a reducing agent in chemical synthesis, was found to release and accept hydrogen reversibly in a two-step phase change process in 1997. The discovery of destabilization by titanium doping made sodium alanates ($NaAlH_4$, Na_3AlH_6) promising materials for hydrogen storage systems 0], 0]. Sodium alanates reversibly absorb and release hydrogen in a two step recombination and decomposition reaction as shown here:

$$NaH + 1/3Al + 1/2H_2 \Leftrightarrow 1/3Na_3AlH_6 \quad \text{Eq. 1}$$

$$1/3Na_3AlH_6 + 2/3Al + H_2 \Leftrightarrow NaAlH_4. \quad \text{Eq. 2}$$

Although sodium alanates do not meet the US DOE goals 03] for vehicle hydrogen storage performance, these materials provide an opportunity to understand the highly coupled processes that present design challenges for implementation of complex metal hydrides into hydrogen storage systems.

Sodium alanates have been used for up-scaled engineered system development efforts 0], 0]. Most notably, the authors designed, optimized, and demonstrated an automotive-scale hydrogen storage system capable of meeting the drive-cycle requirements of the automobile

in collaboration with General Motors 0]. This program developed key technology to enable the use of metal hydride system for applications with high rates of refueling and aggressive fuel release requirements. The completed system is shown in Figure 1. For this study, a portion of the full-scale system was utilized – a 1.7 kg cylindrical bed measuring 5 cm in diameter and 95 cm long.

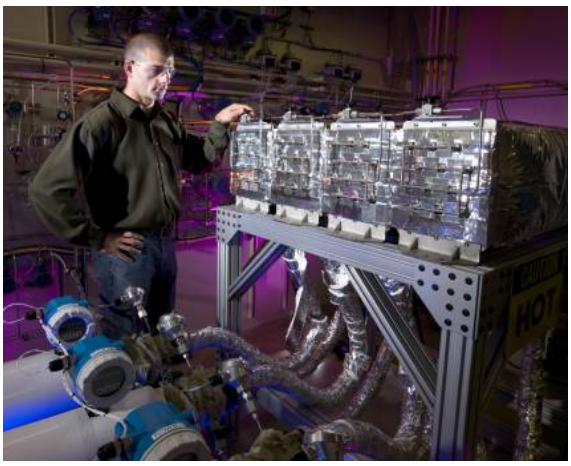

Figure 1: A full scale hydrogen storage system designed for automotive fuelling requirements.

2 Heat Transport, Mass Transport and Kinetics Relations

To facilitate the design and analysis of the up-scaled system, Sandia developed experimentally based models for heat transfer, mass transfer, and chemical kinetics 0]. These models were assembled using physically relevant mathematic expressions with empirically determined coefficients.

A chemical kinetics model was assembled from experimental measurement combined with a geometric representation of the packed particle bed. The model assumed that the equilibrium hydrogen pressures are functions only of temperature and independent of any solid species concentrations. This implies that the various alanate species do not form solid solutions, i.e., they are not intermingled at the molecular level. Reactions between species occur only at interfaces, and the rates of these surface reactions can depend only on gas or surface phase concentrations (and temperature). On the other hand, the volumetric reaction rates within an alanate bed depend on the amounts of the various solid species present, while maintaining thermodynamic consistency. The resulting expressions are outlined in the appendix of Dedrick et al 0].

Permeability was not explicitly measured during the design process of the automotive-scale hydrogen storage system. Upon testing of the full scale system, the authors identified that transport bottlenecks existed due to hydrogen flow limitations in the porous solid. The permeability properties of the compacts at various pressures and temperatures were subsequently quantified and an accurate model was produced that was appropriate for the range of flow regimes present within a hydrogen storage system for automotive applications. A variety of permeability models were investigated for the model development effort. The Young and Todd model was found to fit the requirements of the flow regimes within the

system and was used as a general permeability model. It should be noted that an Ergun expression with Knudsen number modifications would also adequately represent the flow regimes present within the system, but is less suited for modeling multidimensional flows. The Young and Todd model is as follows,

$$K = \frac{\phi}{\tau^2} d_p^2 \left[\frac{1}{32} + \frac{5}{12} Kn \right], \quad \text{Eq. 3}$$

where d_p is the pore diameter and τ is the tortuosity. Porosity is determined through sample mass and volume measurements and tortuosity is determined experimentally. While this model is limited to a characteristic pore diameter, a set of parameters were identified that were appropriate for all relevant flow regimes 0].

The effective thermal conductivity is another important property of the packed hydride material. A large conductivity is desired, which was obtained in the system under study here by using Expanded Natural Graphite (ENG) additives, bed densification, and excess aluminum as thermal conductivity enhancement strategies 0]. The resulting composite material demonstrated an order-of-magnitude improvement in heat transfer performance and was an enabling component to achieving the goals for rapid refueling. The mathematical expression for the enhanced thermal conductivity is represented by the following polynomial in the units of 10^{-2} W/cm-K:

$$k(\psi, E) = 11.7\psi^4 - 32.5\psi^3 + 33.2\psi^2 - 14.8\psi + 40E + 3.4 \quad \text{Eq. 4}$$

where ψ is the fractional hydrogen content (0-1, relative to 4.4 wt%) and E is the weight fraction of ENG flake.

The coupling of each of these models through the energy and momentum equations allows for the prediction of processes within arbitrary bed geometries and operating conditions.

3 Verification at the Application Scale

Verification of the coupled heat transfer, mass transfer, and chemical kinetics models was achieved through two methods; 1) a filling measurement that resulted in the temporally resolved quantity of hydrogen absorbed, and 2) the direct pressure drop measurement across the bed.

The figure below (Figure 2) shows the filling measurement for the hexahydride absorption process. The predicted absorption rate indicates that the bulk permeability is insufficient to resolve the total effective permeability through the bed, indicating a need for a channeling model. A channeling model consisting of 2% of the cross-sectional flow area was found to most closely represent the actual transport within the system observed in experiments [9].

As can be seen in Figure 2, application of the wall-channeling model to the filling measurements under predicts the absorption rate at first (at ~200 s) before over predicting the absorption at later times. The latter discrepancy appears to be due to an over prediction of the capacity of the hydride material, which points to a problem with our kinetics model, while the former discrepancy suggests that our model under predicts the permeability. We focus here on the model permeability issues. In contrast to Figure 2, the comparison shown

in Figure 3 suggests our model over predicts the permeability. Here, four hydride tube vessels were modified to allow hydrogen to flow into the tube on one end and out the other, where a fixed pressure drop was applied to each tube and the flow rate measured. The results show the model over predicts the hydrogen flow rate for a tube temperature of 30°C, although the agreement is better for a tube temperature of 71 °C.

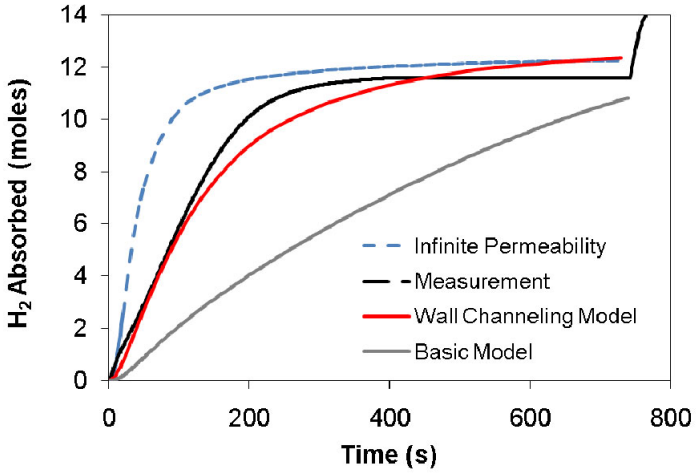

Figure 2: Verification measurements of the coupled models using the large-scale bed. Results indicate that the characteristic permeability of the bed is larger than the bulk permeability of the sodium alanate composite.

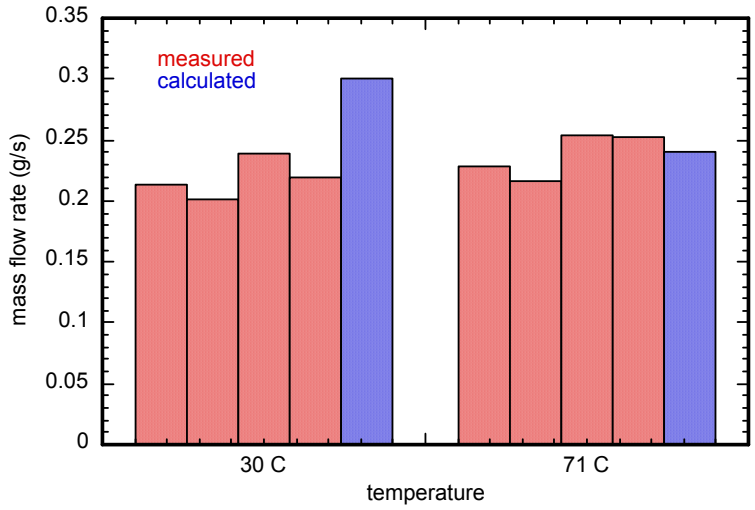

Figure 3: The comparison of measured and calculated mass flow rates for 4 individual tubes is inconsistent.

To investigate the origin of the apparent contradictions shown in Figure 2 and Figure 3 regarding the permeability used in our model, the bed was disassembled to quantify the channeling. Upon removal of the sodium alanate composite, a flow channel of ~0.127 mm was measured indicating that the material had pulled away from the wall and formed a small free flow channel. In addition, significant flow channels were observed to have formed along the near the vessel wall. These were present in the form of both discontinuous fissures and

continuous worm holes (see Figure 4). So, while a wall channel running the length of the tubes is confirmed, the channel we used in the model was too large and should be reduced in size, which would improve the agreement between model and experiment shown in Figure 3. Meanwhile, the fissures and worm holes observed after examining the hydride packed bed provide radial pathways into the material. By including these in the model it would improve the agreement shown in Figure 2 for the absorption rate, without contributing to an over prediction of the flow rate in the axial direction. The combination of these feature changes may likely explain the permeability discrepancy discussed above.

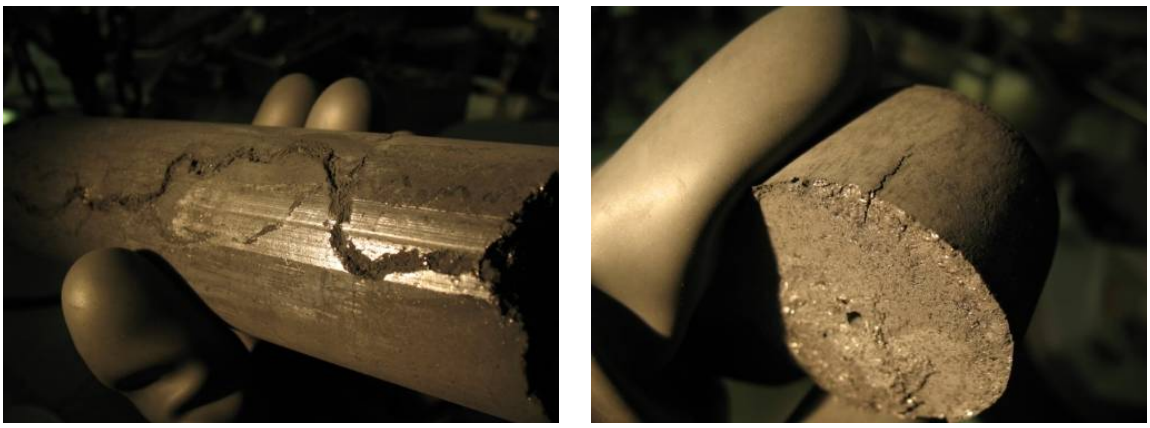

Figure 4: The presence of continuous "wormholes" were observed (left) in addition to discontinuous fissures (right).

4 Design and Optimization Concepts for Future Systems

The detailed understanding of transport within the context of the full scale system allows for the optimization of future designs. Using the models for transport, concepts were developed for the optimization of future systems.

Figure 5 shows two design concepts. The concept on the left represents a cross-section of the bed utilized for this analysis. A single frit exists at the entrance of the vessel. The figure on the right indicates a design concept for improving the permeability of the bed with an annular frit down the center of the bed along the axis.

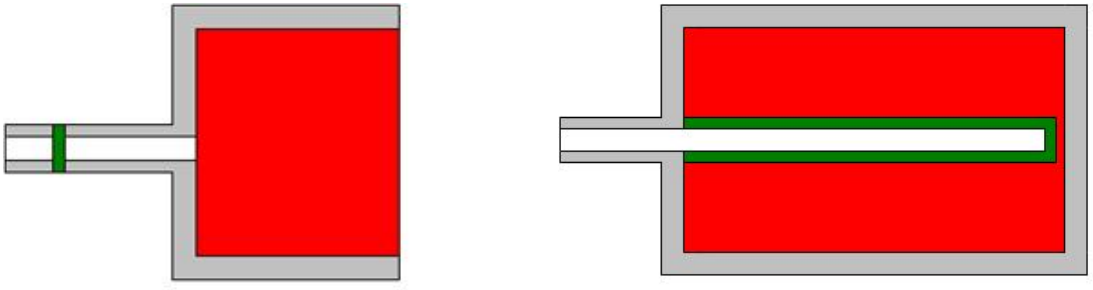

Figure 5: Two bed designs of arbitrary diameter considered for future development. The design on the left utilizes a single frit at the inlet while the design on the right integrates an annular frit along the axis of the bed.

Using the models for heat transfer, mass transfer, and chemical kinetics, the impact of this design feature can be compared on a performance basis to the baseline system. The plot below shows the relative fill speed as a function of vessel diameter. In this case, the Θ refers to the relative rate of hydrogen absorption (Fill Speed) that accounts for the coupled thermodynamics, kinetics, heat transfer, and mass transfer. Three cases are plotted; 1) the thermal-kinetic limit as realized by infinite permeability, 2) the baseline system permeability case, and 3) the axial frit case. For each of the cases, it can be seen that an optimal diameter exists near 3 cm. The fill speed reduction due to permeability is shown in green below the vertical axis and represents the margin for performance improvement with permeability enhancement. The axial frit case approaches the thermal kinetic limit and at larger diameters actually exceeds the performance of the thermal kinetic limit. This seemingly contradictory behavior is due to the added convection cooling effect that increases the effective thermal conductivity of the bed. This convection cooling effect can be exploited in future designs for further system optimization [8]. The above analysis can be performed on systems with more challenging characteristics, such as faster kinetics. These systems behave with the same overall trends; however, the optimal bed diameter is generally smaller.

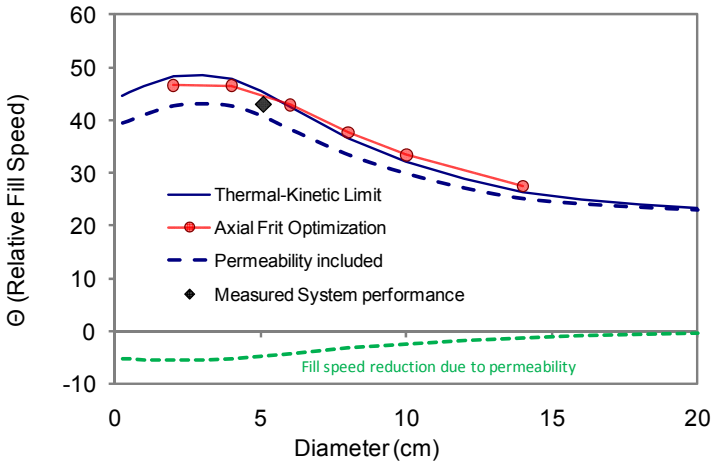

Figure 6: Characteristic fill speed as a function of bed diameter for the two different design concepts in comparison to the infinite permeability case.

5 Conclusions

A fully coupled model of heat transfer, mass transfer, and chemical kinetics has been assembled from experimental measurements for a sodium alanate-based metal hydride system. The coupled models were verified and validated at the relevant automotive scales. Although the coefficients of the individual models are specific to sodium alanates, the same principles can be applied to reactive porous systems in general. The authors utilized these models to quantify the specific transport mechanisms within the sodium alanate complex and subsequently proposed alternative designs that approach the thermo-kinetic limit of the sodium alanate based system.

Acknowledgments

This effort was completed under contract with the USDOE EERE Hydrogen Program. The full scale system was developed under contract with General Motors Research and Development. The authors are indebted to the mechanical design, electrical design and experimental expertise of Ken Stewart, George Sartor, Yon Perras, and Mark Zimmerman, Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94-AL85000.

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