INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 36 (2011) 1578–1591

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

System simulation modeling and heat transfer in sodium alanate based hydrogen storage systems

Mandhapati Raju [a,1], *Sudarshan Kumar* [b,*]

[a] *Optimal CAE Inc., Plymouth, MI 48170, USA*

[b] *Chemical Sciences and Material Systems Laboratory, General Motor R&D Technical Center, Warren, MI 48090, USA*

ARTICLE INFO

Article history:
Received 12 August 2010
Received in revised form
21 October 2010
Accepted 31 October 2010
Available online 24 December 2010

Keywords:
Hydrogen storage
COMSOL model
System model
Sodium alanate
Drive cycle

ABSTRACT

In this paper, we examine the feasibility of an on-board hydrogen storage system using sodium alanate as the hydrogen storage material. A two-dimensional model is used for evaluating refueling dynamics as well as heat transfer coefficients for the system level model. A parametric study is conducted to understand the influence of different operating parameters on the refueling time. System level performance of this storage system during driving conditions is evaluated using a simulation model developed in Matlab/Simulink platform.

1. Introduction

Hydrogen storage is a key enabling technology for hydrogen powered fuel cell vehicles. The U.S. Department of Energy (DOE) [1] has specified important long term targets for hydrogen storage applications based on performance and economic and environmental considerations. Ti-doped sodium alanate [2] has been found to absorb hydrogen reversibly with a maximum theoretical capacity of 5.6%. Hydrogen absorption and desorption in this material can be described as a two-step reaction [3]:

$$NaAlH_4 \leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2 \quad (1)$$

$$1/3Na_3AlH_6 \leftrightarrow NaH + 1/3Al + 1/2H_2 \quad (2)$$

Hydrogen desorption occurs in two stages. First stage is the decomposition of $NaAlH_4$ (sodium aluminum tetrahydride, or the tet phase) and the second stage is the decomposition of Na_3AlH_6 (sodium aluminum hexahydride, or the hex phase). Tet phase decomposition starts at about 60 °C and the hex phase decomposition starts at a relatively higher temperature of 120 °C. Although the theoretical capacity of sodium alanate is 5.6 wt%, practical storage capacity is much smaller. Main reasons for this reduced capacity are (a) limited refueling time for a vehicle (b) presence of additives like Ti and Al to enhance the absorption/desorption characteristics (c) presence of thermal conductivity enhancers, and (d) presence of "isolated islands" [4] of reactants. Luo and Gross [4] report that the maximum hydrogen weight percent in their sample is 3.9%. In this paper we incorporate the kinetics presented by Luo and Gross [4].

Ahluwalia [5] presents assessment analysis for on-board sodium alanate storage system for fuel cell vehicles. The author limits the scope of his study to a "low temperature

* *Corresponding author*. Tel.: +1 586 986 1614; fax: +1 586 986 1910.
E-mail addresses: raju192@gmail.com (M. Raju), sudarshan.kumar@gm.com (S. Kumar).
[1] Tel.: +1 586 986 1365; fax: +1 586 986 1910.
0360-3199/$ – see front matter
doi:10.1016/j.ijhydene.2010.10.100

metal hydride (LTMH) system" which incorporates only the tet phase desorption kinetics. Such a system is limited to a maximum theoretical capacity of 3.7 wt%. However, the actual capacity will be lower than this. This paper aims at evaluating the full storage capacity of the sodium alanate system (including tet phase and hex phase decomposition). Decomposition of hex phase requires a high temperature heating fluid, which in turn requires a burner to heat the heating fluid. Moreover, the desorption kinetics of the hex phase is relatively slow. Hence there is a need for a buffer volume to supply H_2 during periods when the bed is not able to supply sufficient H_2 to the fuel cell. Recent modeling efforts [6,7] of alanate storage systems include a catalytic burner and incorporate both the tet and the hex phase decomposition. A shell and tube heat exchanger is used with the alanate in the tubes and the cooling fluid in the shell.

Detailed heat transfer studies for the alanate system using two-dimensional and three-dimensional models have been done by previous researchers [6,8] for various bed designs. In this work, a different bed design is chosen to study the coupling of heat transfer and chemical kinetics during rapid refueling. A two-dimensional COMSOL [9] model has been developed to simulate refueling of the storage bed. The bed is designed for efficient heat transfer. Alanate is present in the shell and the cooling/heating fluid flows through the tubes. The bed contains 24 cooling tubes. Manifolds are provided at the entrance of the bed to distribute the oil flow to various tubes. Another manifold is provided at the other end of the bed to collect the oil from the tubes. Fins are provided with good interconnectivity between the tubes for enhanced heat transfer within the bed. This design is quite similar to the design used by other researchers [10–12] for high pressure metal hydride storage systems. A similar design has been used by UTRC [8]. In their design, the fins are circular plates placed axially at equal distances. In our design, thermally conductive fins span the entire length of the bed.

Fig. 1 shows a schematic of refueling of the alanate storage bed. Arrangement of the cooling tubes and aluminum fins is shown in a cross-sectional view in Fig. 2. Fig. 3 shows a schematic flow sheet of alanate storage system in a fuel cell vehicle. As shown in Fig. 3, a catalytic burner and buffer tank are included to provide required hydrogen flow to supplement the slow kinetics of the hex phase. System level dynamics of this alanate storage system is analyzed in detail for drive cycle simulations.

The methodology adopted in this paper to evaluate the performance of sodium alanate based hydrogen storage system is as follows. Since heat transfer plays a major role in refueling (shorter time scale compared to desorption phase), a two-dimensional COMSOL model is used to study the refueling dynamics and the temperature distribution inside the bed. A refueling time of 10.5 min is chosen. System performance for various driving cycles is analyzed using a lumped parameter system level model developed in Matlab/Simulink. Initial conditions for the system level model are assumed to be the same as the final state of the bed at the end of refueling. In addition, the system level model requires an accurate estimate of the overall heat transfer coefficient for the chosen bed design. The overall heat transfer coefficient for the system level model is obtained from the COMSOL model as outlined in Section 3.

Storage bed specifications and properties of the metal hydride are presented in Table 1. The alanate sample mixture [4] consists of sodium hydride, aluminum powder and solid titanium tri-chloride in molar ratio of 112:100:4. Crystalline density and bulk density of the material is based on the values reported in literature [6]. Thermal conductivity of the sample mixture can be increased by addition of thermal conductivity enhancers. Thermal conductivity enhancement of up to 8 W/m K has been reported in the literature [6]. Dexcool™ is used as the cooling/heating fluid. Thermal properties of this cooling fluid are provided in [12]. During refueling, the station provides high pressure hydrogen and the cooling fluid. The cooling fluid flows through the tubes and provides cooling to the bed to remove the heat of reaction. Cooling fluid flow rate and temperature can be adjusted to enhance the refueling time.

2. Two-dimensional model for refueling simulations

A two-dimensional cross-section of the bed is modeled for heat transfer. The energy equation is solved for the bed coupled with reaction kinetics neglecting gas phase convection and axial conduction. Bed pressure is assumed to be

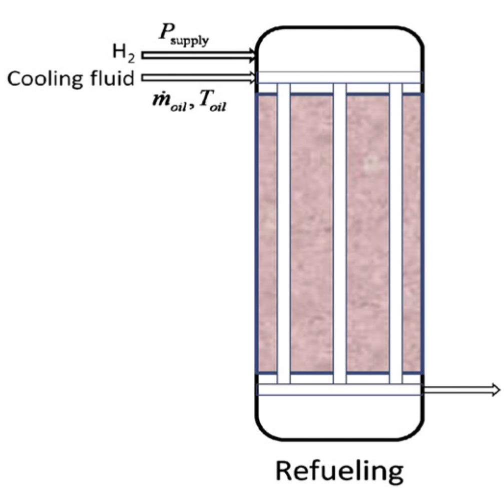

Fig. 1 – Schematic of refueling of Sodium Alanate bed.

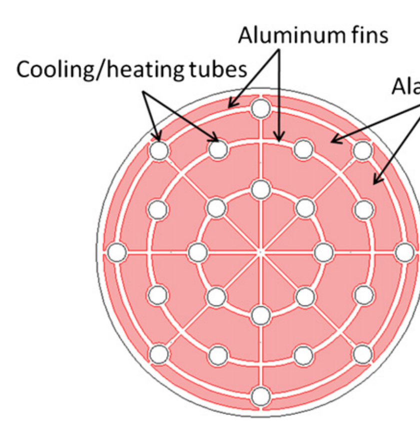

Fig. 2 – Cross-section of the alanate storage bed.