MODELING A METAL HYDRIDE HYDROGEN STORAGE SYSTEM

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Abstract

Metal hydrides have the potential for reversible on-board hydrogen storage and release at low temperatures and pressures. Hence they offer much promise towards an effective hydrogen economy. The following is a study on the theory, modeling, and simulation of the physics and chemistry of hydrogen interactions in a metal hydride bed. The objective was to model the formation of hydride in a metal hydride reactor in 2D. The model considers heat and mass transfer occurring during the hydriding process along with the flow of a cooling fluid. The findings of this study suggest slightly higher hydride formation near the cooler regions as the reaction progresses. This agreed to data available from literature. Overall this paper presents a good test case on hydrogen storage modeling using FEMLAB and lays the ground for further improvements in the model.

Introduction

Hydrogen storage is a key enabling technology for the advancement of hydrogen and fuel cell power technologies. The ability to carry enough hydrogen on-board a vehicle to enable a driving range of greater than 300 miles, within packaging and cost constraints, is the focus of the Department of Energy's hydrogen storage activities [1]. Its target for 2010 for a hydrogen storage system is 6 wt % of the entire system [2]. Storage in the form of hydrides is one of the options being considered. Metal hydrides have the potential for reversible on-board hydrogen storage and release at low temperatures and pressures [3, 4]. Theory, modeling, and simulation will enable the understanding of the physics and chemistry of hydrogen interactions at the appropriate size scale. It will also further the ability to simulate, predict, and design materials to enhance their performance [5].

Hydrogen storage in a hydride bed is a complex process including heat and mass transfer, fluid flow and chemical reactions which include the hydriding and dehydriding kinetics. Figure 1 is a schematic of a kind of metal hydride hydrogen storage vessel which in this case contains Aluminum as well [3]. Literature [3, 4, 6-22] provides evidence that mathematical modeling of hydrogen storage in metal hydride beds have received considerable attention over the past 10 years. Jemni and Nasrallah presented a theoretical study of the mass and heat transfer dynamics in a metal hydride reactor [10]. In subsequent papers they validated their assumptions as well as presented experimental approaches to determine the reaction kinetics, equilibrium condition and transport properties in a $LaNi_5$-H_2 system [11, 19]. Nakagawa *et. al.* presented a 2-D model for the transient heat and mass transfer within a metal hydride bed [18]. *Matt et. al* and Aldas *et. al* besides work on lanthanum beds also presented an integrated model of heat and mass transfer, reaction kinetics and fluid dynamics in a hydride bed [6, 16, 17, 21]. Kaplan and

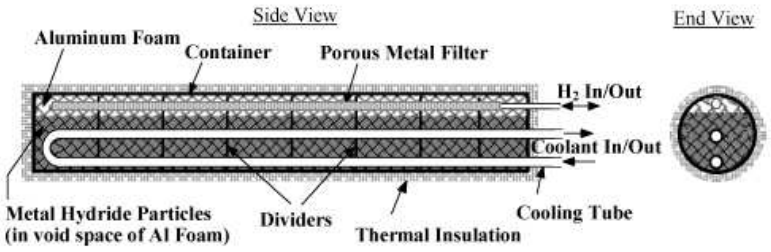


Figure 1
Schematic of the Savannah River National Laboratory metal hydride hydrogen storage vessel

Veziroglu investigated numerically the hydrogen storage process in a 2-D metal hydride bed including the full momentum balance equation [22]. Kikkinedes *et. al* presented a detailed mathematical model which included both the axial and radial dimensions of the storage bed [14]. Apart from the heat and mass transfer effects, a cooling medium for the system was modeled and optimized by them.

The objective of this modeling study is to understand the process by first reproducing some of the results through a 2-D model.

Governing Equations

A two dimensional metal hydride reactor is considered as shown in Figure2. The system mirrors the experimental configuration of Jemni *et al.* [10-12] and that of Kaplan *et al.* [22]. The reactor has a 50 mm inner diameter and 100 mm height and filled with crushed $LaNi_5$ alloy. A cooling fluid is used to remove the energy released during the hydriding process and the heat transfer coefficient h_w between the bed wall and the cooling fluid is assumed to be constant.

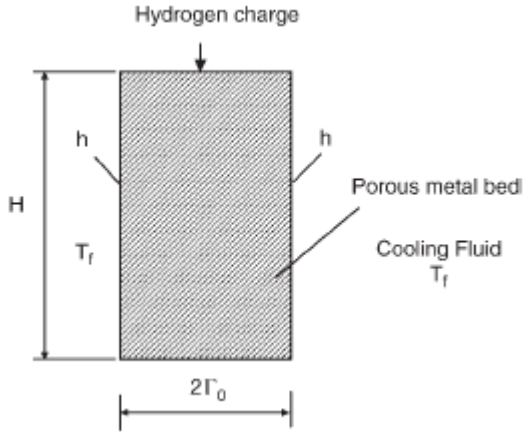


Figure 2
Schematic sketch of the reactor considered

The following are the equations governing the heat and mass transfer and chemical reaction within the hydrogen storage bed:

Energy equation

$$(\rho C_{pg})_e \frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}(r\lambda_e \frac{\partial T}{\partial r}) + \frac{\partial}{\partial z}(\lambda_e \frac{\partial T}{\partial z}) - \rho C_{pg} v \frac{\partial T}{\partial r}$$

$$- \rho C_{pg} w \frac{\partial T}{\partial z} - \dot{m}[\Delta H^o - T(C_{pg} - C_{ps})]$$

The aforesaid continuum equation was obtained assuming thermal equilibrium between the storage bed and hydrogen. Here ρ, C_p and λ_e are the effective density,

specific heat and thermal conductivity respectively. Additional nomenclature can be found in Appendix A. $(\rho C_p)_e$ is calculated as

$$(\rho C_p)_e = \in \rho_g C_{pg} + (1-\in)\rho_s C_{ps}$$

where, $\in$ is the porosity.

The effective thermal conductivity is expressed as

$$\lambda_e = \in \lambda_g + (1-\in)\lambda_s$$

where, λ_g and λ_s are the thermal effective conductivities of the gas and solid phases, respectively.

Momentum equation

The gas velocity can be expressed by Darcy's law:

$$\vec{V}_g = -\frac{k}{\mu_g} g\vec{r}ad(P_g)$$

Hydrogen mass balance

$$\in \frac{\partial(\rho_g)}{\partial t} + \mathrm{div}(\rho_g V_g) = -\dot{m}$$

Hydrogen is assumed to obey the perfect gas law equation $P_g = \rho_g T_g R / M_g$ where R is the universal gas constant and M_g is the molecular weight of hydrogen.

Reaction kinetic

The amount of hydrogen absorbed is given by

$$\dot{m} = -C_a \exp(-\frac{E_a}{RT_s}) \ln(\frac{P_g}{P_{eq}})(\rho_{ss} - \rho_s)$$

where C_a is a material dependent constant, ρ_{ss} is the density of the solid phase at saturation and P_{eq} is the equilibrium pressure calculated using the Van't Hoff relationship:

$$\ln P_{eq} = A - \frac{B}{T}$$

where A and B are material constants obtained from literature [12]

Initial and boundary conditions

The hydride bed is initially assumed to have constant temperature and pressure and hydrogen is assumed to be at rest. Mathematically,

At t = 0

$P = P_o$ $T = T_o$ $v = w = 0$

The boundary walls are assumed to be impermeable and no slip conditions are valid at the boundary walls. The reaction heat is removed from the boundary walls with a cooling fluid whose temperature is T_f. Hydrogen is charged at z = 0 with constant pressure, P_o and constant temperature T_o. The boundary conditions can be expressed as

at r = 0, $\frac{\partial T}{\partial r}(z,0,t) = 0$

at z = 0, $-\lambda \frac{\partial T}{\partial z}(0,r,t) = h_1(T_0 - T)$

at r = Γ_0, $-\lambda \frac{\partial T}{\partial z}(z,\Gamma_0,t) = h_2(T - T_f)$

at z = H, $-\lambda \frac{\partial T}{\partial z}(H,r,t) = h_2(T - T_f)$

where h_1 and h_2 are the heat transfer coefficients between hydride bed and hydrogen gas and between the boundary walls and the cooling fluid respectively.

Problem formulation and solution using FEMLAB

The problem was formulated in a FEMLAB model incorporating “Darcy’s Law”, “Convection & Conduction” and “Convection & Diffusion” modes.

A 2D axis-symmetric model was considered. A rectangle representing half of the mid-section of the reactor was generated (1m by 0.5m). The momentum equations and mass balance equations were coupled through the Darcy’s law mode to get a single equation of the form $\frac{dp}{dx} = A\frac{d^2p}{dx^2}$. Subsequently the energy balance and the mass of the hydride formed was modeled using the “convection & conduction” and “convection & diffusion” modes by incorporating the necessary terms to represent the governing

equations. Where necessary the parameters have been calculated using established correlations.

The solution was obtained by solving the three systems of equations. Initially, a coarse mesh was selected which was subsequently refined (8032 elements) till the computer ran out of available memory. The eventual result yielded estimates of the temperature and pressure variation and the concentration of the metal hydride.

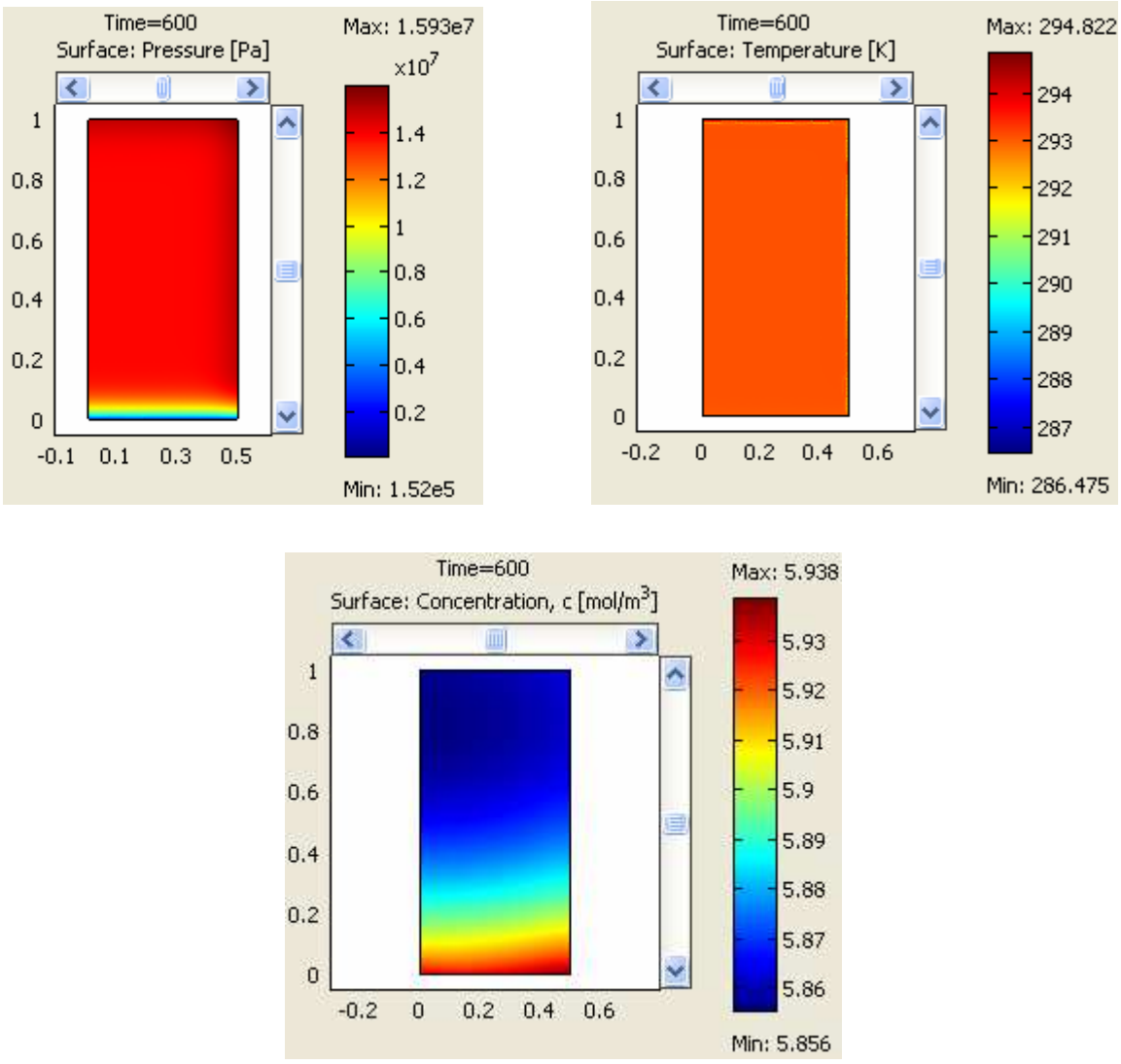


Figure 3

Pressure, temperature and concentration variation in the metal hydride reactor.

Figure 3 shows the results obtained from the FEMLAB solution. After 600 seconds, it is seen that the pressure and the temperature become uniform for most part of the reactor. The concentration of hydride formed is also shown. It is relatively higher towards the cooled boundaries in comparison with the central part. This is in agreement with the data present in literature [22]. Figure 4 shows the variation of the concentration showing greater formation of hydrides closer to the cooled boundaries. The cell peclet number which is the ratio of advective terms to diffusive terms should nominally be less than 10. It was within this range for this model.

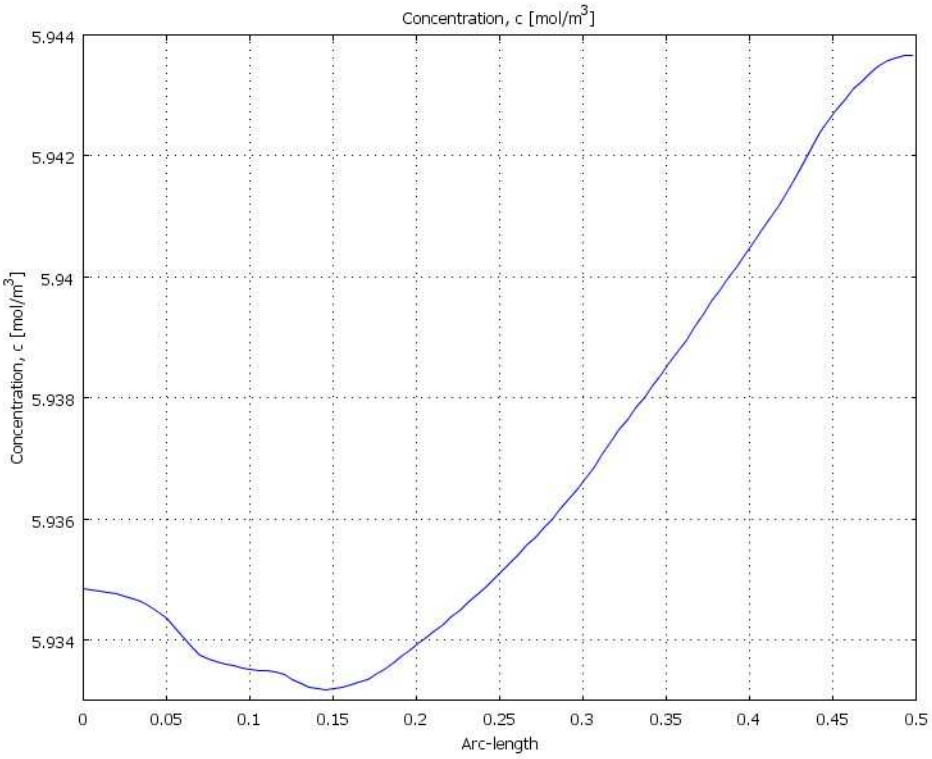
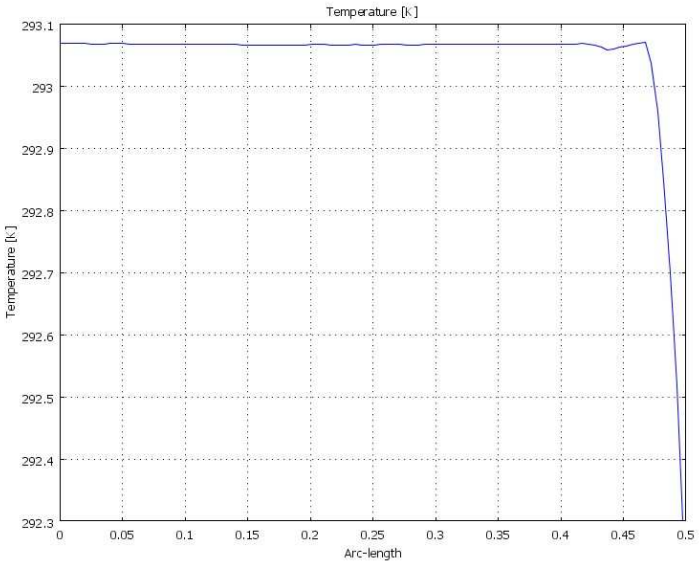


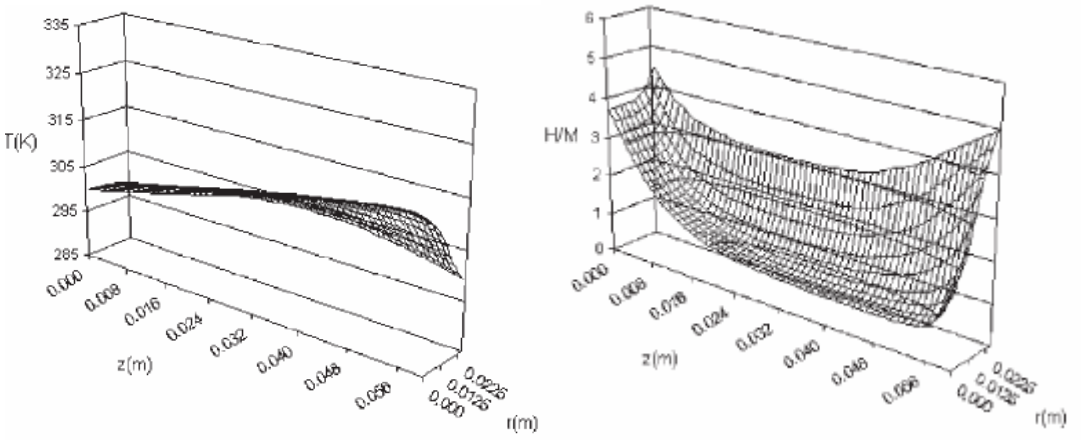
Figure 4
Concentration of hydride formed along the axial direction. Cooled walls have relatively higher concentrations.

Validation/Parametric Study

Validation is an important part of a model. This model was compared to similar work done in the literature. Though not entirely in agreement, the temperature profile was similar to what was reported in a 3D model in literature as shown in Figure 5.



(a)



(b) (c)

Figure 5
Similar temperature profiles of the model (a) and as found in literature (b)[22]
(c) shows the hydride formation in the bed.

The hydride formation profile observed (Figure 4) in the model is similar to what has been reported in the literature (Figure 5c)

For the parametric study, the temperature of the hydride bed was varied. Two cases were considered. Figures 5 and 6 illustrate the variation in the concentration of hydride formed. It is proportional to the amount of heat in the bed and this agrees with literature data, thereby adding in to validate the model.

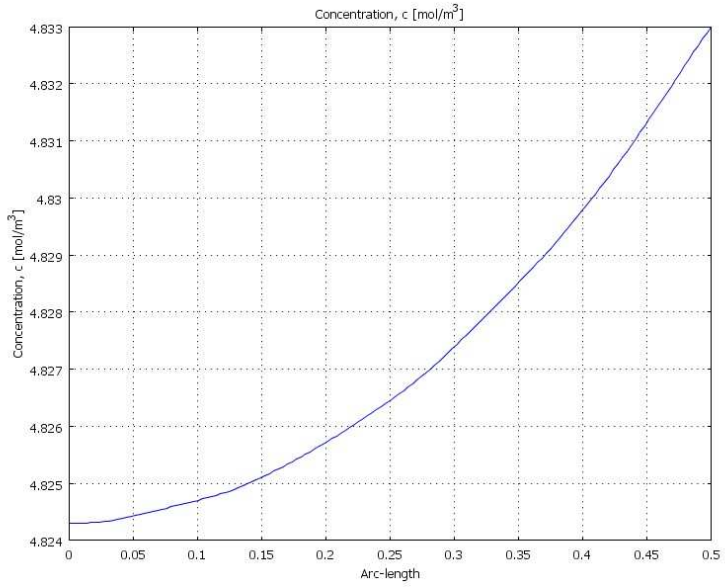


Figure 6
Concentration of hydride formed in the reactor when the temperature is decreased by a factor of 10. Hydride formation decreases.

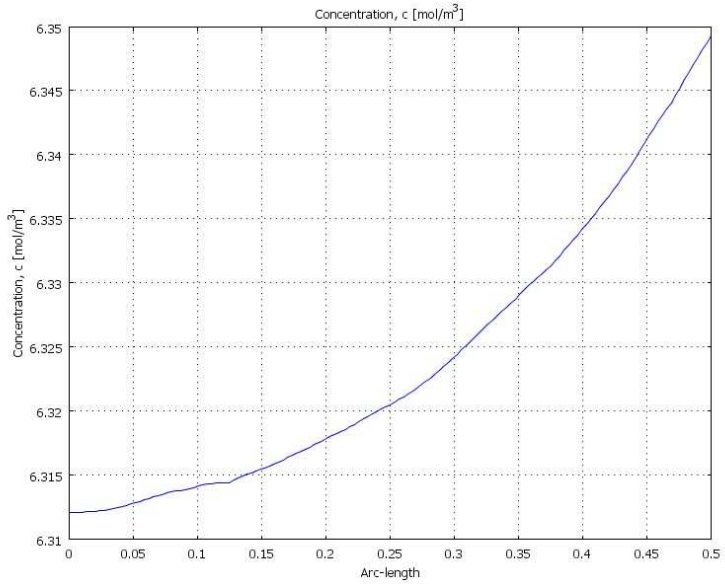


Figure 7
Concentration of hydride formed in the reactor when the temperature is increased by a factor of 10. Hydride formation increases.

Conclusion

In this study the groundwork for modeling hydrogen storage in metal hydrides was investigated. The effect of a cooling fluid too was incorporated. However the model is still at a preliminary stage and needs to be built upon. The effect of temperature on hydride formation was shown to agree with literature and hence the importance of the cooling fluid was demonstrated. The model also successfully presents hydriding behavior similar to that available from literature data.

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Appendix A

Nomenclature

A	= material constant
B	= material constant
C_a	= material constant
C_p	= specific heat
E_a	= activation energy
h	= heat transfer coefficient
H	= reactor height
k	= permeability
$\dot{m}$	= hydrogen mass absorbed
M	= molecular weight
P	= pressure
r	= radial co-ordinate
R	= universal gas constant
t	= time
T	= temperature
v	= velocity component in radial direction
w	= velocity component in axial direction
z	= axial co-ordinate
ΔH^0	= reaction heat of formation
$\in$	= porosity
λ	= thermal conductivity
μ	= dynamic viscosity
ρ	= density
ϕ	= generic variable that representing the variable solved (i.e. u,v,T)
Γ	= exchange coefficient
Γ_0	= radius of hydride bed

Subscripts

e	= effective
eq	= equilibrium
f	= cooling fluid
g	= gas
0	= initial
s	= solid
ss	= saturated