Energy Conversion and Management 173 (2018) 113–122

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Hydrogen storage on $LaNi_{5-x}Sn_x$. Experimental and phenomenological Model-based analysis

D.G. Oliva[a], M. Fuentes[a], E.M. Borzone[b], G.O. Meyer[b,c], P.A. Aguirre[a,*]

[a] Instituto de Desarrollo y Diseño (INGAR), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). Avellaneda 3657, S3002GJC Santa Fe, Argentina
[b] Comisión Nacional de Energía Atómica, Centro Atómico Bariloche, Av. Bustillo 9500, S.C. de Bariloche, Argentina
[c] Instituto Balseiro, Universidad Nacional de Cuyo, CONICET, Argentina

ARTICLE INFO

Keywords:
Hydrogen storage
Hydrogen solid storage
Hydride-forming metals
Mathematical model
Process modelling, simulation and optimization

ABSTRACT

Three hydride-forming metals ($LaNi_5$, $LaNi_{4.73}Sn_{0.27}$, and $LaNi_{4.55}Sn_{0.45}$) have been studied as solid phase hydrogen storage material in batch experiments using pure hydrogen and temperatures ranging from 300 K to 340 K. This process mainly involves: physisorption of hydrogen gas molecules; chemisorption and dissociation of hydrogen molecules; surface penetration of hydrogen atoms; hydride formation; and diffusion of hydrogen atoms through hydride-forming metal. In case the material is fully hydrided, hydride formation ceases and diffusion proceeds on the fully hydrided material.

A phenomenological model was developed by aggregating the first four mechanisms in a single sorption kinetic term involving a first-order driving force, the remaining mechanism being the atomic diffusion in the hydride-forming material. The driving force is computed between external partial pressure and equilibrium pressure according to the Pressure-Composition-Temperature model (PCT). The corresponding parameters for an empirical PCT were estimated from equilibrium data. This equation is more suitable for process engineering optimization due to the smoothness in its concentration domain. Specific sorption rate and diffusion coefficients of the process were also estimated from dynamic data. From a sensitivity analysis, productivity proved to be related to particle diameter. In the frame of batch processes, the global rate is dominated by the sorption kinetic term at the beginning of the experiments with the material being free from hydride, whereas with more than 5–10% of the material being hydrided, diffusion dominates the process. $LaNi_5$ shows higher hydrogen storage capacity than $LaNi_{4.73}Sn_{0.27}$ and $LaNi_{4.55}Sn_{0.45}$ within the investigated temperature and pressure ranges. Diffusion and sorption kinetic limited regions were identified from a sensitivity analysis of process productivity and normalized marginal values. The present work is oriented to modeling, designing, and optimizing storage and purification devices.

1. Introduction

Future energy networks based on hydrogen as a carrier have been proposed in several previous works [1–10]. The storage process is a key component in these networks. Depending on the final application, several technologies have been studied and compared in the literature [11–18]. More specifically, hydrogen storage in hydride-forming materials (HFM) has been extensively investigated. Storage and purification are important concerns in the development of this energy carrier [19–24]. $LaNi_{5-x}Sn_x$ alloys are good HFM candidates because of their low pressure and good global kinetic rates at room temperature. Furthermore, they present high cycling stability and good volumetric capacities [25–30].

Kinetics of these metal hydrides has been studied in order to map the reaction mechanisms of hydrogen charge and discharge and identify possible rate limiting steps [25]. A simplified model obtained by aggregating all mechanisms in only one kinetic expression was previously used by our work team [31,32]. It was embedded in an optimization model for hydrogen purification process design, including charge, venting, and discharge stages. Apparent activation energies are rarely reported; and there exist discrepancies as regards which steps are suggested for controlling the overall rate [33]. So, there is considerable interest in the literature about kinetics models for designers to optimize devices design and model their performance within some ranges of pressure and temperature for a specific application.

Hydrogen storage process mainly involves: physisorption of hydrogen gas molecules; chemisorption and dissociation of hydrogen molecules; surface penetration of hydrogen atoms; hydride formation

---

[*] Corresponding author.
E-mail address: paguir@santafe-conicet.gov.ar (P.A. Aguirre).

https://doi.org/10.1016/j.enconman.2018.07.041
Received 8 May 2018; Received in revised form 10 July 2018; Accepted 13 July 2018
0196-8904/

Nomenclature

C	atomic H concentration [mol cm^{-3}]
D	diffusion coefficient [cm^{2} s^{-1}]
H	Henry constant [mol cm^{-3} MPa^{-1}]
ΔH	enthalpy variation [J mol^{-1}]
P	pressure [MPa]
R	universal gas constant [J mol^{-1} K^{-1}]
T	temperature [K]
V	volume [cm^{3}]
a	parameter [cm^{6} mol^{-2}]
b	parameter [mol cm^{-3}]
c	parameter [mol cm^{-3} K^{-1}]
d	parameter
k	specific sorption rate coefficient [mol MPa^{-1} cm^{-2} s^{-1}]
n	substance quantity [mol]
t	time [s]
v	sorption rate [mol s^{-1}]
gr	slope (parameter) of PCT curve

Subscripts

eq	equilibrium
exp	experimental
H_2	hydrogen
i	index
i_f	cardinality of i
in	initial
l	layer
m	medium, average
r	reactor

Greeks

α	equilibrium pressure factor
β	equilibrium pressure factor
γ	equilibrium pressure factor
δ	binary parameter
ε	binary parameter
ρ	binary parameter

and diffusion of hydrogen atoms through hydride-forming metal. In case the material is fully hydrided, hydride formation ceases and diffusion proceeds on the fully hydrided material [34].

In this work, a phenomenological model is proposed by aggregating the first four mechanisms above described in a single kinetic term involving first-order driving force, the remaining mechanism being atomic diffusion in the hydride-forming material. Thermodynamic equilibrium between gas phase and solid phase imposes a relationship between hydrogen potential in the gas phase and solid phase. The potential in the gas phase is assumed to be the partial pressure of hydrogen whereas the potential in solid phase is assumed proportional to the atomic hydrogen concentration in the solid phase. Equilibrium pressures as a function of atomic hydrogen concentration in the inner side of the gas/solid interphase correspond to the so called PCT diagram [26,35–37]. The driving force is computed between external partial pressure and equilibrium pressure according to the PCT model.

The qualitative behavior of PCT curves has been exhaustively described. Three main zones are distinguished. Initially, a low amount of hydrogen is dissolved in the metal structure for low pressure values. At higher pressure values, dissolved hydrogen evolves into a nucleation form. Then, the ordered phase is formed. In this region, the isotherm shows a plateau behavior; and its length indicates the amount of hydrogen that can be stored by means of an insignificant pressure change. This plateau pressure gains outstanding importance in engineering applications. For higher pressure values, only the ordered atomic phase is present in the metal hydride alloy. In this region, isotherm behavior changes; and incremental pressure leads to an insignificant increase of stored hydrogen. In previous works, [31,32], equilibrium pressure models representing partial profiles of PCT diagram were used. Some authors try to fit total curve by using several equations and thus they obtain a discontinuous function which cannot be used directly in optimization studies [38,39]. Here, HFM equilibrium pressure has been modeled using a single empirical function for a temperature range of 288 K to 388 K, achieving an overall representation of PCT curve that is suitable for optimization problems.

Parameter estimations of the PCT model were performed using both available data in the literature and our own experimental equilibrium values. Once PCT parameters were obtained, specific sorption rate and diffusion coefficients (k and D) are estimated using the proposed phenomenological model, PCT representation and our own experimental data. Dynamical experiments were carried out with pure hydrogen at temperature ranging from 300 K to 340 K and under different pressure values.

The paper is organized as follows: experimental setup is detailed in Section 2; the mathematical model is presented in Section 3; model results and limitations are discussed in Section 4; and finally, conclusions are drawn in Section 5.

2. Experimental setup

Three samples of LaNi$_{5-x}$Sn$_x$ alloys (LaNi$_5$, LaNi$_{4.73}$Sn$_{0.27}$ and LaNi$_{4.55}$Sn$_{0.45}$) were prepared. The alloys were prepared by arc melting under Ar, starting from the pure elements La (99.9%), Ni (99.95%), and Sn (99%). Alloys were remelted several times in order to improve their homogeneity. The resulting buttons, of about 10 g each, were then heat-treated at 1223 K for 48 h in individual quartz capsules containing Ar atmosphere. Chemical composition values were determined by atomic absorption spectroscopy. For details of the sample preparation procedure and alloys characteristics, see Ref. [33].

Sieverts-type volumetric equipment is used for these experiments. The reactor volume (about 7·10^{-3} L) was previously calibrated. Fig. 1 represents the scheme used to measure hydrogen pressure into the

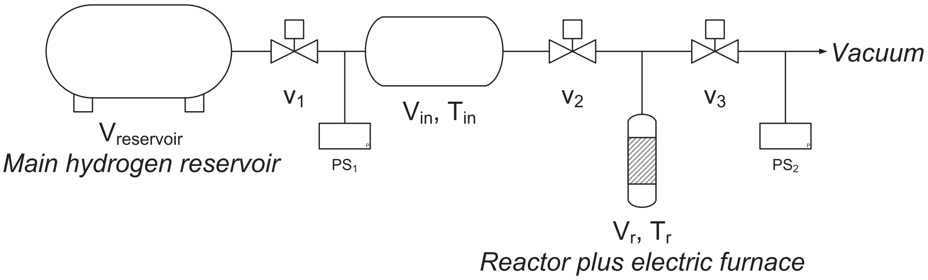

Fig. 1. Experimental setup of the hydrogen storage and discharge system.