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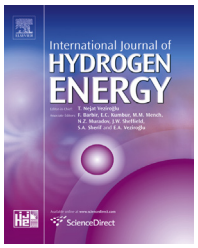

Review Article

A review of mathematical modelling of metal-hydride systems for hydrogen storage applications

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ABSTRACT

Metal-hydrides have been of great interest as one of the most promising materials for hydrogen storage applications. For widespread use, the most appropriate container and thermal management systems to minimise the time of absorption and desorption and maximise the amount of stored hydrogen must be designed. In recent years, many attempts have been made to identify the relationship between different operating and design variables and the resultant performance of metal-hydride systems. In this review, features of mathematical models of metal-hydride reactors including the assumptions, different applied equations and solution methods which have been developed in previous studies are presented. The evolution of the reactor geometries and configurations of cooling systems as well as different effective factors of metal-hydride performance are also discussed.

Introduction

There is an increasing awareness of the adverse effects of greenhouse gas emissions on global warming and climate change due to the use of fossil fuels. Hydrogen is an appropriate alternative to conventional fuels because of its natural abundance and high energy density or heating value per unit mass as well as being environmentally friendly [1]. Widespread uptake of hydrogen energy has yet not occurred because of difficulties with storage since the gas has low energy density per unit volume requiring a large space to be stored at ambient conditions. Methods to address this problem include compressed gas at high pressure (700 bar) or liquid at cryogenic temperatures (20 K), however, both of these methods entail additional costs due to high pressure containment or maintenance of cryogenic temperatures [2].

Metal-hydrides (MH) are able to store relatively large amounts of hydrogen in a solid phase with safety and long-term stability. This class of solid-state materials has advantageous features for hydrogen storage and has been the subject of intensive research since the 1970's [3]. Metal-hydrides are characterised by the following reversible reaction.

$$xM + \frac{y}{2}H_2 \Leftrightarrow M_xH_y + \Delta H \quad (1)$$

where ΔH is the heat of the reaction.

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Nomenclature

T	temperature, K
P	pressure, bar
ρ	density, kg/m^3
$\vec{v}$	velocity vector, m/s
u	component of velocity vector, m/s
ΔH	enthalpy of formation, J/kg
ΔS	entropy change J/kg K
E	activation energy, J/kg
U	Internal energy, J/kg
Q	Heat added or removed, W/m^3
$\vec{q}$	Heat flux by conduction, W/m^2
λ	Thermal conductivity, W/m K
R_g	universal gas constant, J/mol$_{H2}$ K
C_p	Specific heat capacity, J/kg K
H_{gs}	convection coefficient between solid and gas, W/m^2 K
m	hydrogen mass absorbed or desorbed, kg/m^3 s
H/M	hydrogen to metal ratio
Re	Reynolds number
Pr	Prandtl number
μ	viscosity, kg/m K
d_p	mean particle diameter, m
R	reactor internal radius, m
h	reactor length, m
V	volume, m^3
$\overrightarrow{\overrightarrow{\tau}}$	viscous stress tensor, kg/m.s^2
ζ	reacted fraction
E_p	expansion coefficient
ϕ	slope factor
$\varphi_\circ$	slope constant
β	hysteresis factor
ω	averaging volume, m^3
k	permeability m^2
ε	porosity
A	solid gas exchange surface area, m^2/m^3
$\vec{n}$	outward surface normal vector
t	time, s
$\psi_{viscous}$	viscous heat generation rate, W/m^3

Subscripts

a	absorption
d	desorption
e	effective
s	solid phase
g	gas phase
r	radial
z	axial
eq	equilibrium
i	initial

The necessity of modelling

Designing a practical metal-hydride storage system with respect to the different aspects of thermodynamics, kinetics and mass and energy transport requires credible modelling that is in a good agreement with the conditions experienced. Mathematical modelling is a useful tool to identify and predict the state of the metal-hydride during absorption and desorption as well as to determine the relationship between different effective factors with the aim of finding the best performance of the MH storage system.

Many models for one-dimensional [4–7], two-dimensional [8–12] and three-dimensional [13–16] systems have been developed and used to determine transport properties, equilibrium conditions and reaction kinetics of metal-hydride systems. The three-dimensional form of the model requires significantly more time and computing capacity to run and is often only used to investigate those effects that the two dimensional models cannot [15].

Many variables such as the inlet temperature, pressure and hydrogen concentration and flow rate as well as reactor geometry, thermal management system configuration and operating conditions have a significant impact on the performance of MH tanks. Cycling time and the amount of hydrogen to be stored are the main parameters used to measure the overall performance of a hydrogen storage system. However, temperature and pressure evolution as a function of time and space, gas velocity, pressure, temperature and hydrogen concentration distribution in the bed are also necessary to identify the behaviour of MH systems. To reduce the complexity of the model and to reduce computer processing time, assumptions and simplifications are frequently made.

There are a number of review papers specifically about MH reactors and thermal management systems [3,17,18] but these are primarily focussed on experimental and technical aspects of the tank and cooling system designs. This paper presents the different theoretical points of view for mathematical modelling of MH tanks including the various assumptions and simplifications made, variables and equations used as well as the different boundary and initial conditions and numerical methods used to resolve the governing equations. The majority of the important geometrical and operational parameters of the tank and thermal management system which have been considered in previous studies are discussed here.

Storage materials

While the metal hydride material used to store the hydrogen typically does not determine the fundamental equations used to model the storage system, details of properties of the storage material are required in some equations to accurately model aspects such as thermal conductivity and the thermodynamics and kinetics of the interaction of the material with hydrogen.

The material used may be a simple metal, such as magnesium, an intermetallic or alloy, including Mg_2Ni and the AB_5 alloys (of which $LaNi_5$ is the archetypal intermetallic) and AB_2 alloys, and the complex hydrides such as alanates (especially $NaAlH_4$) and borohydrides, such as $Mg(BH_4)_2$. Each of these material classes has advantages and disadvantages. Simple, light metals have moderate gravimetric hydrogen capacities but often have high enthalpy of creation of the hydride, necessitating high temperatures for hydrogen release. Intermetallics can significantly lower the thermodynamics, but