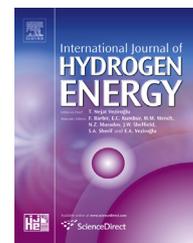


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Adsorption–desorption cycle thermodynamics for adsorptive hydrogen storage system

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ABSTRACT

The thermodynamic characteristics, such as temperature and pressure evolutions, of hydrogen storage systems are important to evaluate and optimize their performance. The thermodynamic models of hydrogen storage systems based on mass and energy balance equations can be expressed simply as lumped parameter or zero-dimensional models. Based on the authors' previous work on the charge–discharge cycle thermodynamics for gaseous hydrogen storage system, this article deals with an adsorption–desorption cycle thermodynamics for adsorptive hydrogen storage system, in which the reservoir is packed with porous adsorptive particles. For simplicity, the hydrogen adsorption amount is assumed proportional with the amount of gaseous hydrogen. Thus, the temperature and the pressure can be solved analytically and therefore can be used for validating the numerical models, e.g. Matlab/Simulink model, theoretically. The thermodynamic models described in this article are useful for developing more detailed multi-dimensional models or more general system level models. The examples given in this article may be served as benchmarks for system level simulations or computational fluid dynamics (CFD) simulations.

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Introduction

The thermodynamic characteristics, such as temperature and pressure evolutions, of hydrogen storage systems are important to evaluate and optimize their performance and to help to make choice for the application among different options [1]. The thermodynamic models of hydrogen storage systems are based on the mass and energy balance equations which are derived from the principles of mass and energy

conservations of thermodynamics. To strength the dynamic characteristics of hydrogen storage systems, the thermodynamic models are expressed as simplified as lumped parameter or zero-dimensional (0D) models which are presented as a set of ordinary differential equations (ODEs). They are fundamentals of distributed parameter or multi-dimensional models, such as a computational fluid dynamics (CFD) model, which are presented as a set of partial differential equations (PDEs). In addition to the fundamental thermodynamic balance equations, the thermodynamic

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Nomenclature			
a_f	heat transfer coefficient between hydrogen and ambient fluid, W/m ² /K	\dot{m}_{out}	hydrogen mass outflow rate for discharge, kg/s
A_s	internal surface area of tank, m ²	M_{H_2}	molecular weight of hydrogen, $M_{H_2} = 2.0159 \times 10^{-3}$ kg/mol
c_p	constant-pressure specific heat of hydrogen, J/kg/K	p	pressure of hydrogen in tank, MPa
c_s	specific heat of adsorbent, J/kg/K	\dot{Q}	heat source term of energy equation, $\dot{Q} = \dot{Q}_a + \dot{Q}_f$, W
c_v	constant-volume specific heat of hydrogen, J/kg/K	\dot{Q}_a	adsorption heat generation rate, W
c_{va}	constant-volume specific heat of hydrogen in adsorbed phase, J/kg/K	\dot{Q}_f	heat inflow rate, W
c_{vg}	constant-volume specific heat of hydrogen in gaseous phase, J/kg/K	R	universal gas constant, $R = 8.314$ J/K/mol
h	specific enthalpy of hydrogen, J/kg	t	time, s
h_{in}	specific enthalpy of inflow hydrogen, J/kg	t^*	characteristic time, s
h_{out}	specific enthalpy of outflow hydrogen, J/kg	T	temperature of hydrogen in tank, K
h_{∞}	specific enthalpy of either inflow or outflow hydrogen, J/kg	T_0	initial temperature in tank, K
k_a	ratio of adsorbed phase mass to the gaseous phase mass	T_a	adsorption contributed temperature, K
m	total hydrogen mass in tank, kg	T_f	temperature of ambient fluid, K
m_0	initial hydrogen mass, kg	T^*	characteristic temperature, K
m_a	hydrogen mass in adsorbed phase, kg	T_{∞}	constant inflow or outflow hydrogen temperature, K
m_g	hydrogen mass in gaseous phase, kg	u	specific internal energy, J/kg
m_s	mass of adsorbent, kg	V_t	internal volume of tank, m ³
\dot{m}	hydrogen mass flow rate, an algebraic quantity, $\dot{m} = \dot{m}_{in}$ for charge process, $\dot{m} = -\dot{m}_{out}$ for discharge process, kg/s	Z	compressibility factor
\dot{m}_{in}	hydrogen mass inflow rate for charge, kg/s	Greek symbols	
		α	dimensionless heat transfer coefficient, $\alpha = a_f A_s / c_v \dot{m}$
		γ	$\gamma = c_p / c_v$
		τ	dimensionless time, $\tau = t / t^*$

models for hydrogen storage system should also include at least hydrogen gas equation of state (EOS), and maybe an adsorption isotherms equation for adsorptive hydrogen storage system or a pressure/composition/temperature (PCT) equation for a metal hydride system. This article starts from very simple thermodynamic system, such as a reservoir for charging and discharging gaseous hydrogen, in which the temperature and the pressure can be solved analytically and therefore can be used for validating the numerical modes, e.g. Matlab/Simulink model, theoretically. The thermodynamic models described in this article are useful for developing more detailed multi-dimensional models or more general system level models. The examples given in this presentation may be served as benchmarks for system level simulations or CFD simulations. This work may be extended to deal with the cases in which the blank reservoir is replaced by a porous one packed with non-adsorptive and adsorptive particles, or even with reactive particles such as metal hydrides.

Heat and mass transfer analysis based on the computational fluid dynamics were widely performed for hydrogen storage systems based on compression [2] and adsorption in activated carbon [3] and metal-organic framework [4].

Thermodynamic analyses for hydrogen storage system were also conducted by some researchers. Yang et al. carried out an analysis of thermodynamic processes involving gaseous hydrogen [5] and a thermodynamic analysis of refueling of a hydrogen tank [6]. Ahluwalia et al. analyzed the dynamics of cryogenic hydrogen storage [7] and cryo-

adsorption hydrogen storage [8] in insulated pressure vessels for automotive applications. Kumar et al. developed a lumped parameter model for cryo-adsorber hydrogen storage tank [9]. The authors of this paper have developed a lumped parameter model for charge–discharge cycle of adsorptive hydrogen storage system [10], and have applied it to a cryo-adsorptive hydrogen storage system [11]. Sphaier et al. [12–14] developed lumped parameter models, with suitability analysis and accuracy improvement, for performance assessment of adsorbed natural gas storage.

It is necessary to find some simple benchmarks to test and validated the numerical method and model of hydrogen storage system. Unfortunately, there is lack of such simple benchmarks. The authors' previous work [15] has obtained analytical solutions for the compression hydrogen storage system considering a tank with neglectable wall thickness, and associated heat capacity and conductive resistance. Yang [16] proposed an approximated method for obtaining explicit analytical expression of equilibrium system pressure based a linear functional form of adsorption amount with gaseous hydrogen amount under low hydrogen loadings.

This article deals with an adsorption–desorption cycle thermodynamics for adsorptive hydrogen storage system, in which the reservoir is packed with porous adsorptive particles. For simplicity, the hydrogen adsorption amount is assumed proportional with the amount of gaseous hydrogen. Thus, the temperature and the pressure can be solved analytically and therefore can be used for validating the numerical models, e.g. Matlab/Simulink model, theoretically.

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