Simulation of hydrogen storage tank packed with metal-organic framework

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ABSTRACT

Hydrogen adsorption in high surface metal-organic framework (MOF) has generated significant interest over the past decade. We studied hydrogen storage processes of MOF-5 hydrogen storage systems with adsorbents of both the MOF-5 powder (0.13 g/cm^3) and its compacted tablet (0.30 g/cm^3). The charge–discharge cycles of the two MOF-5 adsorbents were simulated and compared with activated carbon. The physical model is based on mass, momentum and energy conservation equations of the adsorbent-adsorbate system composed of gaseous and adsorbed hydrogen, adsorbent bed and tank wall. The adsorption process was modeled using a modified Dubinin–Astakov (D–A) adsorption isotherm and its associated variational heat of adsorption. The model was implemented by means of finite element analysis software Comsol Multiphysics™, and the system simulation platform Matlab/Simulink™. The thermal average temperature from Comsol simulation is used to fill the gap between the system model and the multi-dimensional models. The heat and mass transfer feature of the model was validated by the experiments of activated carbon, the simulated pressure and temperatures are in good agreement with the experimental results. The model was further validated by the metal-organic framework of Cu-BTC and is being extended its application to MOF-5 in this study. The maximum pressure in the powder MOF-5 tank is much higher than that in the activated carbon tank due to the lower adsorbent density of MOF-5 and resulting lower hydrogen adsorption. The maximum pressure in the compacted MOF-5 tank is a little bit lower than that in the activated carbon tank due to the higher adsorbent density and resulting higher hydrogen adsorption. The temperature swings during the charge–discharge cycle of both MOF-5 tanks are higher than that of the activated carbon tank. These are caused mainly by pressure work in the powder MOF-5 tank and by adsorption heat in the compacted MOF-5 tank. For both MOF-5 hydrogen storage systems, the lumped parameter models implemented by Simulink agree well with experimental pressures and with pressures and thermal average temperatures from Comsol simulation.

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Nomenclature

ΔH	isosteric heat of adsorption, J/mol
c_{pg}	specific heat capacity of hydrogen gas, J/(kg K)
c_{ps}	specific heat capacity of adsorbent, J/(kg K)
h_w	heat transfer coefficient, W/(m^2 K)
h_i	specific enthalpy of inflow hydrogen flow, J/kg
h_e	specific enthalpy of outflow hydrogen flow, J/kg
k_{eff}	effective thermal conductivity of activated carbon bed, W/(m K)
k_g	thermal conductivity of hydrogen gas, W/(m K)
k_s	thermal conductivity of adsorbent, W/(m K)
M_{H2}	Molecular mass of hydrogen, kg/mol
m_a	mass of adsorbed phase hydrogen, kg
m_g	mass of gas phase hydrogen, kg
m_t	total mass of hydrogen in tank, kg
n_a	absolute adsorption amount per unit adsorbent, mol/kg
n_0	limit adsorption amount per unit adsorbent, mol/kg

p	pressure, Pa
Q	adsorption heat, W/m^3
U	total internal energy, W
W	pressure work, W/m^3
R	universal gas constant, 8.314 J/(mol K)
T	temperature, K
$\vec{v}$	Darcy velocity vector, m/s

Greek symbols

α_{D-A}	enthalpic factor, J/mol
β_{D-A}	entropic factor, J/(mol K)
β_T	volume expansion coefficient, 1/K
ε_b	bed porosity
Φ	viscous dissipation, W/m^3
κ	permeability, m^2
μ	dynamic viscosity of hydrogen, Pa s
ρ_g	density of hydrogen gas, kg/m^3
ρ_p	particle density of adsorbent, kg/m^3

1. Introduction

Hydrogen storage is a bottleneck for the widespread usage of hydrogen as an energy carrier. Hydrogen adsorption in high surface metal-organic framework (MOF) has generated a significant amount of interest over the past decade due to its high gravimetric storage density, fast kinetics and complete reversibility. The metal-organic framework MOF-5 has attracted significant attention due to its ability to store large quantities of hydrogen, by mass, up to 10 wt.% absolute at 70 bar and 77 K, and the increased volumetric hydrogen uptake of MOF-5 will be achieved by powder densification [1,2].

A number of researches about adsorptive hydrogen storage on metal-organic frameworks (MOFs) have been carried out in recent years. Peng et al. [3] used the computational fluid dynamics (CFD) method to simulate the charge and discharge cycle of MOF-5 hydrogen storage system. The low thermal conductivity of the metal-organic framework MOF-5 could limit performances in applications requiring rapid gas uptake and release, so Liu et al. [4] systematically studied the impacts of varying expanded natural graphite (ENG) content and compact density on the thermal conductivity, surface area, specific heat capacity, and crystallinity of densified MOF-5/ENG composites. Juan et al. [5] compared the hydrogen storage capacity of three adsorbents including two activated carbons and a metal-organic framework (MOF-5) on gravimetric and volumetric bases. Schlichtenmayer et al. [6] compared the hydrogen adsorption properties of the two most promising materials for a hydrogen cryo-adsorption tank, AX-21_33 and MOF-177, over a wide range of pressures and at cryogenic temperatures. Lozar et al. [7] compared the capacity of two activated carbons and MOF-5 for storing gases (H$_2$, CH$_4$, and CO$_2$) at different temperatures (77 K and room temperature) and pressures (from 0.1 MPa to 20 MPa). Hirscher et al. [8] studied the hydrogen storage properties for a variety of metal-organic frameworks possessing different structures

and compositions. They claimed that the maximum hydrogen uptake in MOFs is determined by the specific surface area. Kumar et al. [9] developed a quasi-static lumped parameter model for the cryo-adsorption (MOF-5) fuel tank, and discussed the results for the slower processes i.e. discharge, dormancy and venting, and described an alternative solution method for dormancy and venting based on the thermodynamic state description.

In this work we studied hydrogen storage processes of MOF-5 hydrogen storage systems with adsorbents of both the MOF-5 powder (0.13 g/cm^3) and its compacted tablet (0.30 g/cm^3). The charge–discharge cycles of these two MOF-5 adsorbents are simulated and compared with activated carbon. The physical model is based on mass, momentum and energy conservation equations of the adsorbent-adsorbate system composed of gaseous and adsorbed hydrogen, adsorbent bed and tank wall. The adsorption process was modeled using a modified Dubinin–Astakov (D–A) adsorption isotherm and its associated variable heat of adsorption. The model was implemented by means of finite element analysis software Comsol Multiphysics™, and the system simulation platform Matlab/Simulink™.

2. Models of transport and adsorption phenomena

2.1. Distributed parameter model

Mass conservation equation can be written as:

$$\frac{\partial\left(\varepsilon_b \rho_g\right)}{\partial t} + \nabla\cdot\left(\rho_g \vec{v}\right) = S_m \tag{1}$$

The mass source term S_m due to adsorption or desorption can be expressed as: