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Effect of *para*–*ortho* conversion on hydrogen storage system performance

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ABSTRACT

We present a study of the effects of *para*–*ortho* conversion on performance of an adsorption-based hydrogen storage system using finite element methods implemented in COMSOL Multiphysics 4.3a platform. The base model which does not take into account the *para*–*ortho* conversion is validated using the experimental data of Maxsorb activated carbon measured with a test bench at room and cryogenic temperatures. The validated model is subsequently applied to simulate the storage system filled with MOF-5 and then extended to investigate the effects of endothermic *para*–*ortho* conversion of hydrogen isomers on storage and thermal performances during hydrogen charging/discharging cycle for four inlet temperatures, 35, 50, 77 and 100 K. Our results show that the endothermic conversion reduces the system temperature and increases the net storage capacity. The temperature changes due to the different heat sources are used to investigate the effect of conversion on the temperature reduction. The adsorbed and gas phase masses in the storage system with and without conversion at the end of the charging time are used to determine the effect of conversion on the storage system capacity. Even though the conversion is more significant at low temperature (35 K), the gains are larger at high temperature (100 K).

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Introduction

Sorptive hydrogen storage in which hydrogen is physisorbed on high surface area porous materials, such as metal organic frameworks (MOFs) is widely recognized as a promising option for automobile energy storage applications [1]. In order for these technologies to be feasible for on-board applications, the adsorption-based hydrogen storage systems must meet certain specific system-level performance criteria [2]. Even though several MOFs can achieve the storage

densities necessary for on-board applications purely on the basis of their adsorption capacity, it is evident that any realistic hydrogen storage system built using these MOFs cannot readily meet all required system performance targets [3]. This is because the overall performance of a storage system not only depends on material's hydrogen storage densities, but also on the storage and thermal behaviour of the entire storage system, which includes the storage material as well as other structural components, such as tank, heat transfer materials, heating elements, valves, sensors etc. [4].

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Computational fluid dynamics (CFD) simulation is a powerful tool that can help us quickly forecast a storage system's performance without actually relying on routine bench-level experiments, which are complex, time-consuming and requires high-level safety infrastructures and large quantities of sorbent materials. In recent years, CFD has allowed the prediction of system performance of hydrogen storage tanks filled with MOF-5 and Cu-BTC [5]. The authors adapted a previously developed 2D axisymmetric model that was originally validated using experimental data of activated carbon Maxsorb. Irrespective of the temperature conditions imposed in these simulations and others [2,5], the hydrogen gas is typically treated as “normal hydrogen” whose hydrogen's nuclear spin isomers composition of 75% *ortho* and 25% *para*-hydrogen [6], which is the composition at room temperature. Below the room temperature, the composition of *para*-*ortho* fraction present in the hydrogen is defined as equilibrium hydrogen. The composition of these isomers is known to evolve to 100% *para* form as the temperature decreases to 20 K. In the absence of catalysts, however, the conversion follows slow kinetics and takes as many as several days to complete. Recently, in a year-long project, Petitpas et al. conducted several experiments to study the kinetics of natural *para*-*ortho* conversion in a full scale 345 bar automotive cryogenic pressure vessel filled with liquid *para*-hydrogen [7]. The authors reported that the natural conversion started in 10–15 days and it was completed with 25–30 days. Peng and Ahluwalia developed a dynamic model which accounted endothermic natural *para* to *ortho* conversion kinetics to study the dormancy performance and hydrogen loss from an insulated pressure vessel filled with liquid *para* hydrogen [8]. The model predicted that the hydrogen loss rate during the dormancy stage was decreased through the reduced pressure and temperature condition due to the endothermic *para*-*ortho* conversion.

The existing discussions reveal that the strong paramagnetic moment of catalyst cause rapid conversion [9–11]. Fitzgerald et al. found that MOF-74 has a magnetic moment that causes conversion in the hydrogen. The authors observed that this conversion occurs on the order of a minute, whereas conversion is a slow process for hydrogen adsorbed on MOF-5 [12,13]. In the present model, we assumed that MOF-5 has enough catalytic activity to make instantaneous conversion of adsorbed hydrogen. Our assumption is valid under the condition that the paramagnetic moment of pristine MOF-5 could be increased by embedding the paramagnetic particles in the MOF-5, for example, using the method discussed by Paolo et al. [14]. If foreign particles that can catalyse the conversion are embedded in the MOF-5, the overall thermal performance of the hydrogen storage system may have non-trivial contributions from endothermic heat of conversion. For example, the *para*-*ortho* conversion in the equilibrium hydrogen in a storage system filled with MOF-5 at different storage temperatures resulted in temperature swing while recovering the fractions of sorbed hydrogen from the system, as shown by Ahluwalia and co-workers [15]. The authors concluded that an additional external cooling is not necessary for the system to reach theoretical gravimetric and volumetric capacities if the *para*-*ortho* conversion occurs with no kinetic limitations, inside the system containing MOF-5.

The objective of the work presented in this paper is to develop a computational fluid dynamics model that accommodates the endothermic heat of *para*-*ortho* hydrogen conversion in a realistic axisymmetric 2D hydrogen storage tank filled with powder MOF-5 and to understand its effects on overall thermal and storage behaviour of the storage system. In this model, we assume that charged liquid *para* hydrogen converts to equilibrium *para*-*ortho* composition solely as a function of the prevailing pressure and temperature without kinetic limitations [15]. Since no system-level experimental data of MOF-5 adsorption is yet available for validating the model, we validated the base model using the data from bench tests of Maxsorb performed at room temperature and 77 K. Similar methods have been previously adopted by Hardy et al. and Xiao et al. [16,17]. The system of differential equations governing the mass and energy balance in the system subjected to initial and boundary conditions is solved using finite element platform COMSOL Multiphysics 4.3a to obtain the spatio-temporal evolution of heat and mass characteristics. To implement the heat of conversion Q_c , we include the enthalpy of conversion of adsorbed hydrogen in the energy source term. The present model is an attempt to understand the consequences of conversion on charging and discharging by examining an extreme limit, namely maximum conversion effect during the charging time.

Description of the model

We begin with the standard equations of energy and mass conservation to study the multiphysics performance of the storage system. The modified Benedict-Webb-Rubin real gas equation of state, as implemented in NIST REFPROP was used to calculate the thermodynamics properties such as specific heat capacity, density, viscosity and thermal conductivity of *ortho*, *para*, normal and equilibrium hydrogen [18]. The base model which is validated using Maxsorb and the model extension to MOF-5 system does not take into account the *para*-*ortho* conversion heat.

Mass conservation equation and Darcy law

The rate of change of mass of hydrogen entering or leaving the storage tank is described using the Darcy's law of fluid flow in the porous media. This is given by:

$$\frac{\partial}{\partial t}(\rho \varepsilon_b) + \nabla \cdot (\rho \vec{u}) = S_m. \quad (1)$$

In Eq. (1), ρ is the density of the hydrogen gas, ε_b and u are the adsorbent bed porosity and the Darcy velocity of gas flow through the adsorbent, respectively. The mass of hydrogen added to the adsorbed phase per unit volume per unit time is given by the mass source term S_m :

$$S_m = -\rho_b M_{H_2} \frac{\partial n_a}{\partial t}, \quad (2)$$

where ρ_b , M_{H_2} and n_a are the adsorbent bed density, molar mass of hydrogen gas and absolute adsorption, respectively. The negative sign of S_m implies that desorption increases the amount of gaseous hydrogen. The Darcy velocity of the

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