Characteristic features of heat and mass transfer in hydrogen energy storage systems

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Abstract. Reversible metal hydrides are efficient solution for energy storage for distributed and autonomous power. Heat transfer is the major limiting factor for performance of metal hydride devices. Exothermic hydrogen absorption creates significant temperature gradients due to low effective thermal conductivity of powdered metal hydride beds. As the result of a strong dependence of absorption equilibrium pressure on temperature, this gradients lead to heat and mass transfer crisis and compositional inhomogeneities with high concentration of hydride phase near heat sinks and low concentration in the hot core of the bed. Development of the compositional inhomogeneities is accompanied by significant pressure drops over the bed, which can be measured experimentally. We performed experiments on hydrogen absorption in 1 kg metal hydride bed of of La0.9Ce0.1Ni5 inside a water cooled reactor during charge at constant hydrogen flow within the range of 10-30 st.L/min at 0.59 MPa. Results show that heat and mass transfer crisis starts, when pressure in the reactor near hydrogen inlet becomes close to supply pressure, while pressure on the other side of the bed is lower by 0.15-0.25 MPa. These results confirm development of the hot core inside the bed, where reaction almost stops due to high temperature.

1. Introduction
Energy storage is the key technology in energy industry development all over the world [1]. Hydrogen energy storage finds its application in distributed and autonomous power as well as in transportation due to high efficiency of hydrogen fuel cells, high storage density, and operational simplicity. Electricity is a competitor for the hydrogen economy due to a higher efficiency pathway; however, use of intermittent renewables within energy systems is a driver for increased hydrogen generation to manage excess electricity generation [2]. Hydrogen has an advantage over batteries, including Li-Ion, for the applications demanding lasting autonomous operation (more than 1 hour), long-duration storage, and enhanced reliability (no self-discharge and special conditioning requirements, although round trip efficiency may be only about 30%) [1].

To increase efficiency of hydrogen energy storage systems we should decrease energy consumption at hydrogen production, purification, and storage. Modern liquid hydrogen generation systems and 350-750 bar hydrogen compressing systems consume respectively up to 30-40% (10-13 kW·h/kg H2) and 20% (6.4 kW·h/kg H2) of the total chemical energy of stored hydrogen (using lowest heating value). Operation and maintenance of such kind of systems in distributed or autonomous power is prevented due to high investment cost of cryogenic and high-pressure equipment, complicated safety measures, and the necessity of staff training.

The systems using solid-state reversible metal hydride hydrogen storage are free from the mentioned disadvantages. The temperatures and pressures of hydride formation processes are close to ambient, and thus decreasing the useful energy spent for the operation of storage system enhances the simplicity of the
system and operational safety. The typical energy spent for the hydride formation reaction varies within the range of 4 - 5 kW·h/kg [3]. The hydrogen sorption process is accompanied by reaction heat evacuation while desorption can be conducted using heat recovered from hydrogen power production unit. Reversible hydrides of intermetallic compounds are advanced materials for hydrogen storage [4].

For the metal hydride devices, heat transfer has been identified as the major limiting factor [5]. Hydrogen absorbing materials in metal hydride devices are usually fine dispersed beds of powder with particles sizes within the range of 1-10 μm, and low effective thermal conductivity (0.1-1 W/m K) which depends on the pressure of the filling gas and on the concentration of hydrogen absorbed in the particles [6]. At present, the main trend in the increase of efficiency is the development of efficient heat exchangers with enhanced surface or the creation of compact high-conductive structures on the base of ballasting materials with high thermal conductivity [7].

The task of the present study is identifying characteristic features of heat and mass transfer inside metal hydride beds to determine bottlenecks in performance enhancement of metal hydride devices. We describe development of a heat and mass transfer crisis as a result of development of a hot core inside a metal hydride bed, and perform experiments on hydrogen absorption in a metal hydride reactor to support our assumption.

2. Generation of composition inhomogeneities at absorption

The hydrogen absorption is an exothermic reaction, which occurs when the supply pressure is greater than the equilibrium pressure $P_s$. Hydrogen flow is determined by the equation:

$$ q = C_a \exp \left( -\frac{E_a}{RT} \right) \left( 1 - \frac{C}{C_{\text{max}}} \right) \ln \left( \frac{P}{P_s} \right) $$

where $C_a$, $E_a$ are the absorption constant and activation energy, $R$ is the gas constant, $C$ is the mass concentration of hydrogen in metal, and $C_{\text{max}}$ is the maximum concentration. The equilibrium pressure is characterized by van’t Hoff equation:

$$ \frac{P}{P_0} = \exp \left( \frac{\Delta S}{R} - \frac{\Delta H}{RT} + \varphi(C) \right) $$

where $P_0$ is the reference pressure (at standard conditions), $\Delta H$ is the enthalpy, $\Delta S$ is the entropy of hydride formation, and $\varphi(C)$ is the function describing dependence of the equilibrium pressure on mass concentration of hydrogen $C$.

Heat and mass processes inside a metal hydride bed are greatly affected by a form of PCT diagram given by (2). In ideal case (figure 1a) the bed has isotherms with flat plateau and uniform temperature distribution. Absorption starts from the point S, hydrogen at the inlet pressure $P_{in}$ reacts with metal, and the reaction heat heats the bed. Equilibrium pressure rises until $P = P_{in}$ (point A). At this moment the reaction slows down as logarithm of pressure ratio in (1) tends to 0. This phenomenon is called heat and mass transfer crisis [8]. The inlet valve can be closed and the bed would be cooled down to temperature $T_w$ at a heat exchanger wall (A to A’), or gradually charged to the final state (point F) at low hydrogen flow (A to F). In real application the process is more complex. The bed has considerable size and due to low effective thermal conductivity the temperature distribution is not uniform inside the bed. There exists a hot core and cold regions near the heat exchanger walls [9], which absorb hydrogen at different rates. The example is presented in figure 1b, where the hot core of the metal hydride bed is rapidly heated up (S to A), while regions near heat exchanger walls are cooler and absorb more hydrogen (S to B). Thus, the crisis moves along the bed from hot regions to cold ones. If the hydrogen inlet is closed, the compositional inhomogeneity is formed inside the bed (A to A’) and (B to B’). The slope of plateaux prevents hydrogen uptake until the bed is cooled down, thus increasing the difference between the regions. Absorption-desorption hysteresis conserves this compositional inhomogeneity over long period of time after equilibration of pressure and temperature inside the bed [10].
Figure 1. Hydrogen absorption inside a metal hydride bed: (a) ideal case with flat plateaux of isotherms; (b) case with plateau slope and non-uniform temperature distribution.

Figure 2 illustrates this phenomenon. At the left a simplified metal hydride bed with 1D symmetry is pictured. Linear size of the bed generally lays within a range from 0.01 to 0.1 m, while particle diameter has the order of magnitude of 10 μm, which results in low effective thermal conductivity of the bed. Hydrogen is supplied from one side of the bed, while the opposite is cooled by heat exchanger. Typical profiles of pressure, temperature and hydrogen concentration in metal are presented in the right side of figure 2. One should expect a significant pressure difference between the hot and cold sides of the bed, which lead to creation of compositional inhomogeneity. This pressure difference can be easily measured, thus the effect can be proved experimentally.

Figure 2. A simple metal hydride bed (left) and scheme of generation of compositional inhomogeneity at absorption of a portion of hydrogen (right).

3. Experiments
Heat and mass transfer during absorption was investigated in a RSP-8 metal hydride reactor (figure 3) [11]. The reactor has tubular design, inner and outer tubes form two liquid heat exchangers with an annular reaction chamber between them, which is filled with 1 kg of La₀.₉Ce₀.₁Ni₅, maximum H₂ capacity is $V_{\text{max}} = 140$ st.L, nominal operating capacity is $V_{\text{nom}} = 110$ st.L.

Hydrogen from the gas ramp was fed into RSP-8 from the top at constant rates $q_0$ ranged from 10 to 50 st.L/min at inlet pressure of 0.59 MPa. The reactor was cooled by tap water at $T_w = 8-9°C$ at 0.2 g/s. The state of charge of the reactor is calculated as:
SoC = \frac{1}{V_{nom}} \int q dt \tag{3}

For desorption, the reactor was heated by tap water at $T_w = 60^\circ C$ at 0.1 g/s, hydrogen was released to atmosphere. Measurements were conducted using Bronkhorst EL-Flow mass flow meter/controller, Aplisens pressure transmitters model PC28, and thin film platinum sensors Heraeus M422, 1 kΩ. The experiments were controlled using LabView software with discretization of 1 Hz.

![Figure 3. The RSP-8 reactor and the scheme of experiments: P – pressure gauge; FR – flow meter/controller](image)

4. Results
For lower charging rates a subcritical regime was observed. Results for $q_0 = 10$ st.L/min are presented in figure 4, the heat and mass transfer crisis is clearly visible both from pressure and hydrogen flow curves. At the start, the reactor is fully discharged. When inlet valve opens, hydrogen fills the reactor and absorption begins all over the metal hydride bed. The flow regulator starts maintaining the hydrogen flow at constant $q_0$. Heat transfer is sufficient and the bed is cooled down from the initial peak temperature. Pressure in the upper part of the reactor starts to rise, while the pressure at the bottom is nearly constant. At the moment when $P_1$ becomes close to $P_{in}$, the flow starts to fall down, which indicates crisis, and after that $P_2$ begins to increase. Subcritical regime lasts 8.6 min, during which 101 st.L is charged (SoC 92%).

In contrast, for $q_0 = 30$ st.L/min (figure 5) crisis occurs immediately after the start, reaction generates too much heat, cooling is insufficient, and there is no region corresponding to constant hydrogen flow. Pressure at the bottom falls down in the beginning, showing that only a part of hydrogen flow reaches the bottom of the reactor and cooling at the bottom is sufficient. Later the hot core enlarges, absorption at the reactor top slows, and more hydrogen reaches the bottom, more heat is generated and pressure $P_2$ starts to increase as well.
Figure 4. Absorption of hydrogen supplied at 10 st.L/min

Figure 5. Absorption of hydrogen supplied at 30 st.L/min
5. Conclusion
Heat transfer is the major limiting factor for performance of metal hydride devices. The main bottleneck is the strong dependence of absorption equilibrium pressure on temperature and the low thermal conductivity of metal hydride beds. Their combination creates significant temperature gradients due to exothermic nature of hydrogen absorption. These gradients lead to heat and mass transfer crisis and compositional inhomogeneities with high concentration of hydride phase near heat sinks and low concentration in the hot core of the bed.

Significant pressure drops accompany the development of the compositional inhomogeneities over the bed. We performed experiments on hydrogen absorption in 1 kg metal hydride bed of La$_{0.9}$Ce$_{0.1}$Ni$_{5}$ inside a water cooled reactor during its charge at constant hydrogen flow within the range of 10-30 st.L/min at 0.59 MPa. Results show that heat and mass transfer crisis starts when pressure in the reactor near hydrogen inlet becomes close to supply pressure, while pressure on the other side of the bed is lower by 0.15-0.25 MPa. These results confirm the development of the hot core inside the bed, where reaction almost stops due to high temperature.

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References
[1] Aneke M and Wang M 2016 Appl. Energ. 179 350-77
[2] Hanley E S, Deane J P and Gallachóir B P Ó 2018 Renew. Sustain. Energ. Rev. 82 3027-45
[3] Sandrock G 1999 J. Alloy. Compd. 293-295 877-88
[4] Lototskyy M V, Tolj I, Pickering L, Sita C, Barbir F and Yartys V 2017 Prog. Nat. Sci-Mat. 27 3-20
[5] Afzal M, Mane R and Sharma P 2017 Int. J. Hydrogen Energ. 42 30661-82
[6] Hahne E and Kallweit J 1998 Int. J. Hydrogen Energ. 23 107-14
[7] Artemov V I, Minko K B and Yan’kov G G 2016 Int. J. Hydrogen Energ. 41 9762-8
[8] Borzenko V, Dunikov D and Malyschenko S 2011 High Temp+ 49 249-56
[9] Blinov D V, Borzenko V I, Dunikov D O and Romanov I A 2014 Int. J. Hydrogen Energ. 39 19361-8
[10] Mohammadshahi S S, Webb T A, Gray E M and Webb C J 2017 Int. J. Hydrogen Energ. 42 6793-800
[11] Dunikov D, Borzenko V, Blinov D, Kazakov A, Lin C Y, Wu S Y and Chu C Y 2016 Int. J. Hydrogen Energ. 41 21787-94