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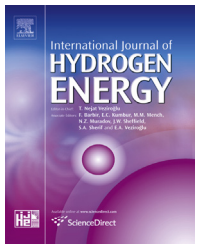

Thermal runaway as a new high-performance method of desorption of hydrogen from hydrides

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ABSTRACT

In this investigation by experiments, it was proved that the thermal runaway can be used as a new high-performance method of desorption of hydrogen from metal-hydrides. On its kinetic and thermodynamic parameters, this method is considerably superior to requirements established by US Department of Energy for onboard hydrogen storage systems. For its processing, the thermal runaway does not require any certain temperature or pressure. It can work at any temperature and pressure of ambiance. The hydrogen desorption by the method of the thermal runaway runs with aid of electrochemical reactions. This is why this process is easily controllable by electrotechnical methods and hence it is far less inertial than the thermal processes used in the traditional thermochemical method of the hydrogen desorption from the metal-hydrides.

Introduction

Currently, a hydrogen storage systems development with necessary parameters is the most challengeable technical problem on the way of a large-scale introduction of the hydrogen energy into every sphere of the world economy [1–3]. The safest and most effective method of hydrogen storing is by using solid media, such as sorbent materials and hydrides [4–7]. However, the specific capacity indexes as well as kinetic and thermodynamic parameters for reversible hydrogen storages are not yet sufficient for practical use. Today many publications are devoted to solving this problem [4–10].

The criteria for an onboard hydrogen storage system have been defined by the US Department of Energy (DOE) in close collaboration with the automotive industry [11]. The most important of them are criteria for those systems' specific capacity and kinetic & thermodynamic parameters. The most frequently quoted 2015 target for specific capacity is a gravimetric storage system by capacity exceeding 5.5 wt%, and volumetric storage system by capacity exceeding 40 kg m^{-3}. Then these performance targets were prolonged up to year 2020.

In our earlier study, it was demonstrated, that as a result of the thermal runaway, large amounts of hydrogen are released [12,13]. The thermal decomposition of electrodes demonstrated that hydrogen is accumulated in the electrodes of nickel–cadmium batteries in the process of their operation. So KSX-25 (nickel–cadmium battery with sintered electrodes by capacity 25 Ah) with the service period of over five years contains approximately 800 L of hydrogen [12,14,15]. The

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capacity of the sintered nickel matrix of the oxide-nickel electrode as a hydrogen absorber was quantified as 20.1 wt% and 400 kg m^{-3} [14]. These values exceed thrice all the earlier data obtained by the traditional methods for any reversible metal hydride [1,10]; also they are far exceed the criteria for hydrogen storage systems established by US DOE. Although the nickel hydrides decomposition runs very slowly (about 140 h at the temperature 800 °C) [12,14,15]. So these hydrides do not satisfy the criteria of US DOE for hydrogen storage systems on their kinetic and thermodynamic parameters.

The criteria established by US DOE for kinetic parameters of onboard hydrogen storage systems are represented in Table 1.

The last three parameters (Table 1) determine limits for inertia of the system.

The first parameter (Table 1) determines a minimum permissible hydrogen release rate for storage systems. It is based on an average 3000 lb current production vehicle, which typically has a powerplant of about 150 kW. This is why this parameter is standardized by power of a powerplant. But for evaluation of kinetics of hydrogen storage systems, it is better to standardize this parameter by a mass or a volume of a system [10]. An average fuel tank volume at cars of this class is approximately 70 L. So the petrol mass makes about 52.5 kg. Thereupon the minimum full flow rate standardized by a mass will make

$$V = 5.714 \times 10^{-5}\ \text{wt\%}\ s^{-1}. \quad (1)$$

In the paper [16], there was evaluated the necessary peak desorption rate for these cars; it makes up to 8.333×10^{-4} wt % s^{-1}.

These kinetic values are quite achievable for modern Mg-based hydrides [17], complex hydrides and their compositions [18]. Although, thermodynamic parameters of these hydrides do not correspond to the requirements established by US DOE.

The criteria established by US DOE for thermodynamic parameters of hydrogen storage systems are as follows: min/max delivery temperature is −40/85 °C; min delivery pressure from storage system (FC = fuel cell, ICE = internal combustion engine) is 3FC/35 ICE bar (abs); max delivery pressure from storage system is 100 bar (abs). For evaluation of hydrides applicability as hydrogen accumulating units, their values are calculated of enthalpy of dehydrogenation. Let us make use of van't Hoff's relation [10].

$$\ln(P) = \Delta H/RT - \Delta S/R \quad (2)$$

Thereupon for enthalpy minimum and maximum, from permissible ranges of temperature and pressure values, we obtain the following estimations: $\Delta H = -43.3$ kJ $mol^{-1}(H_2)$ at ($T = 85$ °C, $P = 3$ bar) and $\Delta H = -21.3$ kJ $mol^{-1}(H_2)$ at ($T = -40$ °C, $P = 100$ bar). In the calculations, it was taken into account that dehydrogenation entropy of different hydrides is approximately equal to -130 J K^{-1} $mol^{-1}(H_2)$ [10]. The hydrides with lower values of the enthalpy require a higher energy consumption for their dehydrogenation, while the hydrides with much higher enthalpy values are not stable and hardly suitable as materials for the hydrogen storage.

Currently, only two methods of hydrogen desorption from hydrides exist, namely thermo-chemical and chemical methods.

As for the thermo-chemical method, a process of hydrogenation/dehydrogenation is determined by setting of certain values of hydrogen's pressure and temperature, i.e.

$$MeH_n \xleftarrow{P_1,T_1} \xrightarrow{P_2,T_2} Me + \frac{n}{2}H_2, \quad (3)$$

where Me is a metal or an alloy being under investigation, P_1, T_1 and P_2, T_2 are pressure and temperature of process of hydrogenation or dehydrogenation respectively.

As for the chemical method, hydrides interact with water with exhalation of hydrogen, i.e.

$$MeH_n + nH_2O \rightarrow Me(OH)_n + nH_2 \quad (4)$$

The reaction (4) allows obtaining twice as much hydrogen than the latter contains in the initial hydride. Although, this reaction is principally irreversible. Besides, it can be conducted only for a limited number of hydrides [19]. A regeneration of initial hydrides for the reaction (4) is principally possible but inexpedient for economical reasons. This is why currently, this method is considered unacceptable for hydrogen storage systems.

In this paper, we propose the thermal runaway as a principally new high-performance method of hydrogen desorption from hydrides. This work aim is studying of kinetic and thermodynamic parameters of thermal runaway as a new method of hydrogen desorption and also comparison of the obtained parameters with correspondent parameters obtained with aid of traditional, i.e. thermo-chemical method and with US DOE requirements. In this paper, the investigations started in the papers [12–15,20–23] were continued.

Table 1 – DOE technical targets: onboard hydrogen storage systems.

Discharging rates	Units	Value
Minimum full-flow rate	(g s^{-1}) kW^{-1}	0.02
Start time to full flow (20 °C)	s	5
Start time to full flow (−20 °C)	s	15
Transient response at operating temperature 10%–90% and 90%–0%	s	0.75

Experimental

For the experiments, the KSX-25 batteries with sintered electrodes by capacity 25 Ah were used. As a result of a long-term operation of those batteries (more than five years), in their electrodes, about 800 L hydrogen is collected [12,14,15]. Hence, batteries with a service life 7 years were used for this study. In the paper [14] by experiment, it was proved that hydrogen is collected in metal-ceramic matrices of these electrodes. Thus, the metal-ceramic matrices of these electrodes represent hydrides of metals. Let us investigate kinetic and thermodynamic parameters of those electrodes as hydrogen accumulating units while using for it the traditional thermo-chemical method and the method of thermal runaway.