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Advanced reactor concept for complex hydrides: Hydrogen absorption from room temperature

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ABSTRACT

Complex hydride materials (CxH) are potential candidates for hydrogen storage in automotive applications due to their high hydrogen storage capacities. However, the reaction rates of these materials are rather low at temperatures below 100 °C implying negative effects on absorption performance e.g. at a fuelling station. In this paper simulated and experimental results of a new reactor concept that can improve the dynamic reactor performance are presented. This concept is based on the combination of a metal hydride (MeH) and a CxH in one reactor, separated by a gas permeable layer. The storage capacity of available MeH materials is just ~1 wt.%, however, they show very high reaction rates even at room temperature. Thus, the idea of this concept is to combine both: the high storage capacity of the CxH material and the high reaction rate of the MeH material. The two reference materials for this study are 2LiNH₂–1.1MgH₂–0.1LiBH₄–3 wt.%ZrCoH₃ (Li–Mg–N–H) and LaNi_{4.3}Al_{0.4}Mn_{0.3} (MeH). In the first part, 2D simulation results are presented showing the development of a reaction front from the core to the annulus of the tubular reactor caused by the fast exothermal absorption reaction of the MeH material. In the second part, experimental results of a 50 g lab-scale reactor and simulated scenarios are presented and used for model validation. In the present scenario it has been possible to reduce the time to initiate the absorption reaction from room temperature by approximately 500 s.

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1. Introduction

For future fuel cell driven cars hydrogen storage still poses a major challenge. The state of the art storage method for conventional vehicles is realized by a pressure tank. However, as the density of gaseous hydrogen is very low, high pressures of up to 700 bar are required accompanied by the corresponding accident risk potential [1]. One out of several alternative technologies to high pressure tanks is hydrogen storage

in solid state hydride materials. In these materials, gaseous hydrogen is bonded to a solid compound, e.g. a metal (M), by a reversible exothermic/endothermic reaction according to:



The advantages of such a solid state hydride material in comparison to the other storage options are the relatively low pressures (<100 bar), the possibility to store hydrogen at ambient temperatures and the reduced amount of free

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Table 1 – Summary of important characteristic properties for MeH and CxH materials [27,35].

	MeH	CxH
Type of reaction	Insertion	Conversion
Thermodynamics	Δ_{RH} from 30 to 40 kJ mol ⁻¹ possible	Δ_{RH} from 30 to 40 kJ mol ⁻¹ possible
Kinetics	Seconds at RT	Minutes/hours at $T < 100$ °C
Capacity	1–2 wt.%	2–18.4 wt.%
Availability	Commercial	Limited, only from research laboratories

hydrogen, as the gaseous hydrogen is bonded to the solid by a chemical reaction.

The existing hydride materials for this solid state hydrogen storage show large variations in their properties and can be classified in different ways. For the reactor concept that is presented in this paper, the following distinction between metal and complex hydride materials is most convenient (compare Table 1) [1].

- 1.) Metal hydride materials absorb hydrogen by an *insertion reaction*. These materials are very well studied in the literature and an important representative is e.g. LaNi₅ [2,3]. The absorption reaction of these materials takes place in the order of seconds even at room temperature and the materials show hydrogen storage capacities below 2 wt.%.
- 2.) Reversible complex hydride materials absorb hydrogen by a *chemical conversion reaction*. This reaction type enables high storage capacities of up to 18.4 wt.% [4], but causes low reaction rates at temperatures below 100 °C [1,5]. These materials have been studied since 1997, when Bogdanović proved the reversibility of NaAlH₄ which became a major representative material for complex hydrides [6] in the consecutive years.

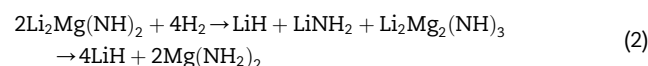
For hydrogen storage applications in automotive systems a high system gravimetric storage density of up to 0.075 kg_{H₂} kg_{system}⁻¹ is crucial (see DOE requirements in Ref. [7]). Therefore, the latter conversion reaction based materials with high theoretical storage capacities on a material level are suitable candidates. However, their low reaction rates at moderate temperatures and pressures will always lead to poor tank dynamics during absorption and desorption processes. Thus, a new reactor design for CxH materials for automotive applications has to focus on an improvement in the dynamic tank behaviour in order to reach the DOE goals for the filling time of 2.5 min for 5 kg_{H₂}. This is a new aspect in reactor design as for many applications and MeH materials the focus in the reactor design was on heat or mass transfer, leading to the development of numerous solutions, e.g. fins, foams, heating coils [8–13] or filters [10,14,15], etc.

In this paper, a new approach to solve this problem is presented that is based on the combination of a MeH material with a Li–Mg–N–H material in one storage reactor. With such a combination, the advantages of both material classes can be used: the high storage capacity of the Li–Mg–N–H material and the improved dynamic behaviour of the reactor due to the MeH material. In the literature, there is only one similar study using a low temperature metal hydride together with magnesium hydride [16]. However, in the present paper, such a combination reactor is studied for the first time using a novel

complex hydride material and a metal hydride material in the same reactor, thus applying the same hydrogen pressures on both materials.

1.1. Selection of representative materials

In order to study this new concept two suitable materials have been selected. As the amount of available, reversible complex hydride materials is limited, this material was defined first. One material that has already been studied on a reactor level is sodium Alanate [8,9,17–19]. This material theoretically absorbs 5.6 wt.% of hydrogen in two steps, however, approx. 4 wt.% reversible storage capacity are experimentally observed, e.g. Ref. [20]. Other materials that are also promising candidates are based on the basic Li–Mg–N–H system [21]. For example the material 2LiNH₂–1.1MgH₂–0.1LiBH₄–3 wt.% ZrCoH₃, that has been presented by Zhang et al., reversibly absorbs approx. 3.5–4 wt.% of hydrogen [22,23] at temperatures below 200 °C. The equation for the absorption reaction of the main Li–Mg-system of this material can be written according to [24] as



This material has been chosen as model material for reactor design in the present study, which is part of activities aiming at a coupling of a storage tank to a HT-PEM fuel cell in technically relevant scale – allowing for 2 h operation at 1 kW_{el}. In the following, the material will be abbreviated with Li–Mg–N–H material. The material has been synthesized by KIT¹ from 2LiNH₂ + MgH₂ requiring a 1st metathesis reaction to 2LiH + Mg(NH₂)₂, before it can reversibly absorb and desorb 3.2 wt.% of hydrogen in ~1 h. Details on this reaction, bulk properties and the reaction rates that are required for the model are published in Ref. [25] and summarized in Table 2.

For a suitable MeH material, the selection is much easier. For instance, there exists a variety of alloys based on LaNi₅ with different additives influencing the thermodynamics of the material [26,27]. For the present study, LaNi_{4.3}Al_{0.4}Mn_{0.3} has been chosen as it shows suitable material properties [28]. In the following, this material will be abbreviated as MeH. It has been purchased from Konik Industries Corporation with a particle size of 50 μm, and the first activation procedure has been performed at <10 bar and RT. The properties of this material have been adapted from LaNi₅ using several reaction rate experiments (not presented here), and all values are summarized in Table 2.

¹ KIT: Karlsruhe Institute of Technology, Institute of Nanotechnology.

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