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Dynamic power supply by hydrogen bound to a liquid organic hydrogen carrier

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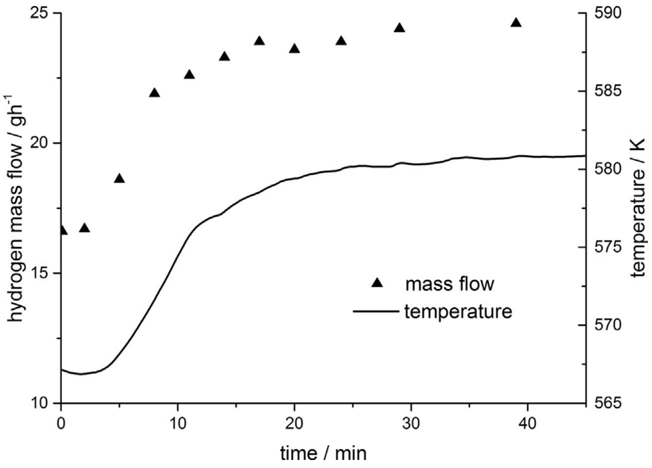
HIGHLIGHTS

- Liquid Organic Hydrogen Carrier can store hydrogen in a dense form.
- Dynamics of hydrogen release are crucial for application in energy storage.
- Capability of reacting to fast changes in energy demand has been evaluated.
- The combined system of release and purification unit can react very fast.

GRAPHICAL ABSTRACT



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ABSTRACT

Liquid Organic Hydrogen Carriers (LOHCs) are able to store hydrogen in a dense and safe form at ambient conditions. While storage of electrical energy in these carrier systems is one possible and attractive application, the dynamics of the load profile has been believed to represent a major challenge for this storage technology. Conversely, we report here that storage systems based on the LOHC technology are indeed able to deal with significant variations in power demand. This is due to the significant free volume in the LOHC release unit offering the opportunity to handle dynamic behavior by pressure changes. While pressure changes allow quick adaption of the power release on demand, changes in the reactor temperature lead to slow modification of the power output, as demonstrated in this work for hydrogen release from perhydro-dibenzyltoluene (H18-DBT).

1. Introduction

Liquid Organic Hydrogen Carriers (LOHCs) represent a promising technology for the storage of hydrogen and have attracted

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rising attention in recent years [1–8]. The approach is based on the reversible hydrogenation of an organic carrier compound. Hydrogen is chemically bound to the carrier, which allows safe and dense storage under ambient conditions. A number of different substances such as toluene [9], *N*-ethylcarbazole [10] or other carbazole derivatives [11] have been described as LOHCs. Due to specific advantageous properties, such as excellent commercial availability, high thermal stability and good hydrogen capacity, the dibenzyltoluene (H0-DBT)/perhydro-dibenzyltoluene (H18-DBT) LOHC system is of special relevance for practical and industrial applications (Scheme 1) [12,13].

Although the LOHC technology can be applied for the transport and storage of hydrogen for chemical utilization, the focus of this work is on the storage of energy, e.g. from renewable sources. For high-quality energy storage applications the storage system needs to be able to react sufficiently fast in response to the fluctuating profiles of power production and power demand. While batteries could potentially act as a power buffer, the capability of the LOHC systems for dynamic operation is still an important parameter to determine the required capacity of the battery.

Both the hydrogen uptake and hydrogen release units consist of four major elements: a chemical reactor, a hydrogen gas purification system, a heat integration system and an electrochemical conversion system (e.g. electrolysis or fuel cell). Even though the dynamics of fuel cells cannot cope with every load change in the millisecond range [14], they can usually react fast enough on transients for most applications and are significantly faster than typical chemical reactors. The main challenge for increasing the hydrogen output from the dehydrogenation reactor is the fast supply of the required heat into the reactor. Increasing the temperature of the reactor takes at least several minutes, depending on the size of the reactor, the power of the heating system and the heat transport conditions in the reactor. Another option to increase the hydrogen production rate is by increasing the volume flow of hydrogenated LOHC through the reactor. This would increase the hydrogen release at the cost of conversion. In this way, a relatively fast increase of hydrogen output is achievable as pumping performance can be adapted quickly. However, system efficiency and effective storage density would decrease in this way.

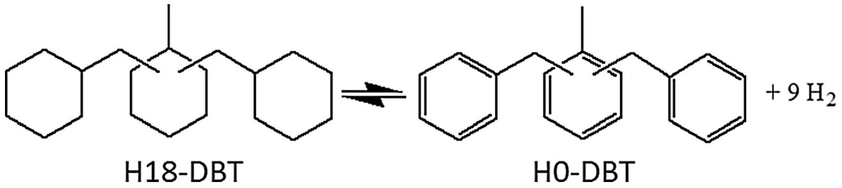
In previous works several of the current authors have published studies on the physicochemical properties of LOHC materials [11,13,15,16], their phase equilibria [17–19] and their environmental and health impact [5]. A number of theoretical studies by different authors have addressed the efficiency of LOHC based energy storage [20–22] and concepts for the application of the LOHC technology [3,6,23–25].

A large proportion of the work on LOHC published so far focuses on catalysis. Amende et al. [26] studied the mechanism of dehydrogenation on Pd(111) surfaces. Spectroscopic studies on the dehydrogenation on Pt(111) have been done by Gleichweit et al. [27]. Matsuda et al. [28] studied the catalysis of dehydrogenation in the liquid phase for a carbazole derivative under ultrahigh vacuum by linking it to an ionic liquid, thus avoiding evaporation. Other works addressed the effects of surface structure on the stability of the LOHC *N*-ethylcarbazole during dehydrogenation [29]. Studies on catalysis and reaction mechanisms of a variety of potential LOHC materials have been published in recent years by Dong et al. [30], Mehranfar et al. [31], Brayton and Jensen [32], Papp et al. [33], Do et al. [34], Li et al. [35], Fujita et al. [36] and other authors.

Nevertheless, the number of experimental works on LOHC and related hydrogen technologies dealing with actual energy storage systems (i.e. at least hydrogen release plus e.g. fuel cell) is limited. First reports on demonstration plants date back to the 1980s. In these works a release unit for dehydrogenating methyl cyclohexane providing hydrogen to a combustion engine is described [37,38]. More recently two companies have reported the construction of demonstration plants based on toluene/methyl cyclohexane in the Japanese cities of Yokohama [39] and Hitachi [40]. However, the dynamics of electricity supply that can be realized with the LOHC units are not addressed in these publications. To the best of our knowledge there are also no other publications, neither on the dynamics of such systems nor on demonstration plants running with more sophisticated LOHCs. Hence, the dynamics possible with a LOHC system based on dibenzyl toluene should be studied for further improving the understanding of this upcoming technology on a system level.

There are some works on metal hydrides touching the issue of dynamics. This is a somewhat related technology for storing hydrogen, since both approaches are based on chemically bound hydrogen and have similar energy demands for hydrogen release. Lototskyy et al. [41] discussed applications for metal hydride based storage and remarked on the respective dynamics. The main limiting factor for fast and dynamic hydrogen release is the heat transfer into the solid material. Laurencelle and Goyette [42] studied the effects of aluminum foam for improving the heat transfer. They concluded that the performance could be significantly improved by introducing these foams. Pasini et al. [43] evaluated metal hydrides concerning the dynamics of hydrogen uptake and concluded that they are insufficient for mobile applications. The solid nature of metal hydrides is one of the major drawbacks for their application for dynamic hydrogen release. Hence, liquid hydrogen carriers might overcome this challenge.

This publication elaborates on the possibility for dynamic operation of LOHC-based hydrogen release units through suitable pressure adjustment in the release unit. If the hydrogen production rate does not perfectly match the consumption rate in the fuel cell, elemental hydrogen accumulates in the sections between the reactor and the fuel cell. Thus, the free volume in the connecting pipes of those sections can act as a pressure buffer increasing the ability for dynamics of the system. The flexibility of the option described is limited towards low pressures by the fact that hydrogen needs to flow into the fuel cell. When pressure decreases, the pressure gradient and subsequently the hydrogen flow decrease as well. Therefore, a minimum pressure has to be maintained. A theoretical maximum of the pressure is determined by Le Chatelier's principle. If the hydrogen pressure is too high dehydrogenation will be limited by its thermodynamical reaction equilibrium. In many cases the maximum pressure will be limited by practical aspects, e.g. by mechanical constraints and safety considerations. However, as will be shown in this paper, only a few hundred millibar of pressure change in the free-volume of the LOHC dehydrogenation unit



Scheme 1. Hydrogen storage and release using the H0-DBT/H18-DBT LOHC system.