Journal of Power Sources 353 (2017) 131–137

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Release of hydrogen from nanoconfined hydrides by application of microwaves

Luis Miguel Sanz-Moral [a], Alexander Navarrete [a], Guido Sturm [b], Guido Link [c], Miriam Rueda [a], Georgios Stefanidis [b, d], Ángel Martín [a, *]

[a] *High Pressure Processes Group, Department of Chemical Engineering and Environmental Technology, University of Valladolid, Doctor Mergelina s/n, 47011 Valladolid, Spain*

[b] *Process & Energy Department, Mechanical, Maritime & Materials Engineering Faculty, Delft University of Technology, Leeghwaterstraat 39, 2628 CB Delft, The Netherlands*

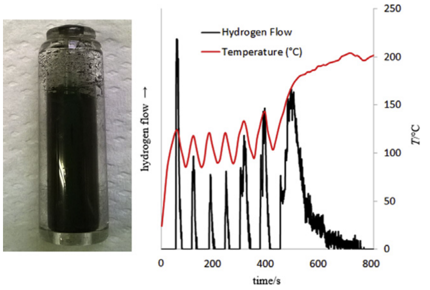
[c] *Institute for Pulsed Power and Microwave Technology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz-1, 76344 Eggenstein-Leopoldshafen, Germany*

[d] *Process Engineering for Sustainable Systems Section, KU Leuven Celestijnenlaan 200f, Box 2424, 3001 Leuven, Belgium*

HIGHLIGHTS

- Hydrogen release from a hydride nanoconfined in C/Si aerogels has been studied.
- Carbon makes the material susceptible to microwave heating.
- Nanoconfinement accelerates hydrogen release kinetics and eliminates induction time.
- With microwave heating fast response to variable hydrogen demands is achieved.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 February 2017
Received in revised form
14 March 2017
Accepted 21 March 2017

Keywords:
Hydrogen storage
Hydride
Microwave heating
Aerogel
Supercritical CO_2

ABSTRACT

The release of hydrogen from solid hydrides by thermolysis can be improved by nanoconfinement of the hydride in a suitable micro/mesoporous support, but the slow heat transfer by conduction through the support can be a limitation. In this work, a C/SiO_2 mesoporous material has been synthesized and employed as matrix for nanoconfinement of hydrides. The matrix showed high surface area and pore volume (386 m^2/g and 1.41 cm^3/g), which enabled the confinement of high concentrations of hydride. Furthermore, by modification of the proportion between C and SiO_2, the dielectric properties of the complex could be modified, making it susceptible to microwave heating. As with this heating method the entire sample is heated simultaneously, the heat transfer resistances associated to conduction were eliminated. To demonstrate this possibility, ethane 1,2-diaminoborane (EDAB) was embedded on the C/SiO_2 matrix at concentrations ranging from 11 to 31%wt using a wet impregnation method, and a device appropriate for hydrogen release from this material by application of microwaves was designed with the aid of a numerical simulation. Hydrogen liberation tests by conventional heating and microwaves were compared, showing that by microwave heating hydrogen release can be initiated and stopped in shorter times.

---

* Corresponding author.
E-mail address: mamaan@iq.uva.es (Á. Martín).

http://dx.doi.org/10.1016/j.jpowsour.2017.03.110
0378-7753/

1. Introduction

The increasing share of solar and wind energy in the energetic mix and the COP21 agreement pave the way for a new family of technologies based on renewable energy [1]. Since these renewable energy forms are fluctuating by its nature, it is necessary to develop technologies for storage of energy in periods of excess supply, to use it during the periods of excess demand. Direct use of these energy forms on onboard applications is also not possible, and requires an intermediate form of energy storage.

Storage of this energy in form of hydrogen is one of the most explored methods. The challenge is being addressed using storage systems based on compressed, liquefied and materials-bounded hydrogen [2]. Compared to gas and liquid storage tanks, solid hydrides can store high amounts of hydrogen in small volumes, which usually are liberated by a reversible chemical reaction by thermolysis. However, currently investigated hydrides are limited by slow hydrogen release kinetics or by high thermodynamic stabilities which make it necessary to apply high temperatures to decompose them [3]. Therefore, one of the technological challenges which restrain the development of hydrides for H_2 storage is the heat transfer inside the storage tanks [4]. Great efforts have been made in order to overcome this problem. However, this issue can be circumvented if heating energy is delivered directly to the material, and not by heat transfer through the storage tank. Application of microwaves offers this possibility.

The decomposition of several metal hydrides under microwave irradiation was studied by Nakamori et al. [5]. They concluded that conductive loss and particle size were the two most important parameters controlling H_2 release. Silva Dupim et al. [6] showed that by particle size reduction an effective heating of the particles was achieved by approximating the size of the particles to the penetration depth of the electromagnetic field in the metallic powder. They obtained this size reduction by applying cold rolling. Another alternative is modifying the dielectric properties of the complex by mixing it with a hydride which actuates as a microwave absorber, as for example $LiBH_4$ [7]. Zhang et al. proposed the use of a honeycomb ceramic monolith coated with 0.54 wt% Ni (corresponding to a thin layer of Ni of 0.2 μm) to hold the hydrides, which allowed the rapid heating of the complex [8].

An alternative to improve the kinetic decomposition of hydrides is using a catalyst [9], but this method adds weight to the complex and sometimes requires the use of expensive metals. Another alternative is the nanoconfinement of the hydride [10,11]. By confining the hydride inside the porous host, hydride particle size is restrained to the pore size, and particle agglomeration and growth process, which could have an adverse effect on the kinetic decomposition, are avoided. Moreover, some porous hosts, like carbon or silica mesoporous materials, chemically interact with different hydrides and destabilize it, further improving the decomposition kinetics [12]. By combination of these effects, the decomposition temperature and release kinetics can be significantly improved by nanoconfinement. On the negative side, the support materials usually employed, such as mesoporous silica, have very low thermal conductivities that slow down the kinetics of hydrogen release if conventional heating by conduction is applied, and the use of a support material also adds weight to the compound.

However, the mesoporous host can be functionalized to provide additional properties to the material [13]. In particular, it can be functionalized to enhance the absorption of microwave energy, and thus combine the main advantages of the two approaches: nanoconfinement and microwave heating. Indeed, a porous material with a high dielectric lost could confine the hydride and change the global dielectric properties of the complex. A material that fulfills this requirement is carbon, which can be manufactured as mesoporous carbon or as carbon aerogel. Some researchers have already confined hydrides like $NaAlH_4$, $LiBH_4$ [14] or $Mg(BH_4)_2$ into carbon scaffolds [15,16]. However, these carbon structures present a limitation which is its low pore volume that restricts the space available for the confinement of hydride inside the support. Due to this limitation, the maximum hydride loadings achieved in carbon matrixes are between 15 and 30% wt., which limits the hydrogen storage capacity below the requirements for practical applications. An alternative could be a hybrid material with leaves more pore space for the confinement of a hydride and provides appropriate global dielectric properties of the complex, making it susceptible to microwave heating. Silica aerogel was already suggested as a very promising material for hydrides confinement due to its remarkable surface properties, and in particular to its high pore volumes that allow confining as much as a 50%wt of hydride [17]. Carbon/silica hybrid aerogels can combine favorable dielectric properties with high pore volumes. Carbon/silica porous materials can easily made by the carbonization of resorcinol–formaldehyde/silica aerogels, as described by Kong et al. [18], keeping favorable textural properties for encapsulation.

In this work, a combined C/SiO_2 porous material susceptible to be heated up by microwaves has been synthesized and impregnated with a hydride. Ethane 1,2-diaminoborane (EDAB) has been chosen as hydride because of its promising properties for H_2 storage: high H_2 content (~10 wt%) and the absence of undesirable volatile impurities in the released gas [19]. Material characterization and H_2 liberation tests by conventional heating and by application of microwaves have been performed in order to evaluate the possible advantages of application of microwave heating in nanoconfined materials. In addition a numerical simulation of the device under microwaves has been performed to reach better understanding of the process.

2. Materials and methods

2.1. Materials

Resorcinol (R, ≥99% purity from Digma-Aldrich), formaldehyde (F, 36.5–38% in H2O from Digma-Aldrich), 3-(aminopropyl)triethoxysilane (APTES, 99% purity from Digma-Aldrich), ethanol (EtOH, 99.5% from Panreac) and technical carbon dioxide (from Carburos Metálicos) were used for the aerogels synthesis. Technical nitrogen (from Carburos Metálicos) was used for the aerogels pyrolysis. Chlorotrimethylsilane (CTMS, ≥98% from Sigma-Aldrich) and methanol (MeOH, 99.8% from Panreac) was used to functionalize the C/SiO_2 particles. EDAB (96%, from Sigma-Aldrich) and MeOH were used for the wet impregnation of samples.

2.2. Complex synthesis

The resorcinol-formaldehyde aerogels were synthesized following the methodology of Kong et al. [18]. Cylindrical monoliths were made by using R:F:APTES:EtOH, in a molar ratio of 1:2:1:60. After gelation the alcogels were dried by using supercritical CO_2 in order to avoid capillary stresses during solvent removal which could damage de aerogel structure. The drying took place in a closed circuit. The alcogels were placed in a chamber which can be isolated from the rest of the circuit. Then CO_2 was pumped till 10.5 MPa and heated till 40 °C. After it the CO_2 was recirculated till the solvent was completely removed. Three loads of fresh CO_2 where needed for a complete drying of the gels. A detailed description of the setup can be found in a previous work [20].

Subsequently the RF/SiO_2 aerogels were pyrolysed in a homemade tubular oven. The samples were heated till 800 °C were the T