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Improving magnesium based systems for efficient hydrogen storage tanks

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ABSTRACT

Development of technologies which utilize hydrogen as energy vector requires the realization of efficient gas storage systems. Materials suitable for hydrogen storage at the solid state have to fulfill some specific requirements in order to be used inside the reactors. First of all it is necessary to have a material which could be cycled without observing reduction of performances in terms of kinetics and total hydrogen capacity. The reaction of the material with hydrogen must be reversible even after long time cycling, i.e. repeated absorption and desorption runs. For what concerns the efficiency of the reactors, one of the main parameters to be taken into account is the thermal conductivity of the bed of hydride. The use of powder is detrimental for thermal conductivity and also for gas permeability and particle entrainment by the gas flow in the reactor. Moreover powders after long term cycling tend to pack and sinter evidencing the problems reported before. For this reason powders of hydrides are compacted, generally in cylindrical shape, after mixing with agents for enhancing thermal conductivity and mechanical stability (for example Al, Cu, carbon-based materials). It has been reported that compacted systems during cycling tend to disaggregate returning to the form of powder in the loose form. This swelling mechanism causes rapid slowdown of the kinetics and all the problems correlated to the use of the powders. For this reason many efforts have been spent in order to extend the life of the compacted systems. In this work it is reported the study performed to improve the preparation of compacted powder systems by a procedure which includes the deposition of a thin layer of a metal on the surface of the pellet. The pellets prepared with this procedure demonstrated, after 50 cycles, variations of dimension eight time lower in comparison to those obtained on pellets prepared without coating. The quantity of metal deposited is less than 0.1% of the weight of the pellet and it doesn't affect hydrogen capacity and kinetics of reaction. Kinetics of reaction and microstructure have been studied with a volumetric Sievert's type apparatus and with Optical and Scanning Electron Microscopy respectively. Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

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Introduction

Hydrogen storage represents one of the main obstacle to widespread diffusion of technologies which make use of hydrogen as energy vector. Requirements which have to be fulfilled by systems for hydrogen storage are mainly hydrogen storage capacity, both gravimetric and volumetric, kinetics, reversibility, long-term cycling. Conventional systems, as storage at high pressure or at low temperature, present problems which have still to be overcome. In the case of hydrogen at high pressure, energy has to be spent in order to compress the gas at more than 700 bar. Tanks with reinforced composites materials have to be realized. In the other case, storing hydrogen at low temperatures, energy has to be spent in order to liquefy the gas. The system have to be open in order to avoid overpressure due to liquid boil off [1]. For this reason storage of hydrogen at the solid state by physisorption and chemisorption has been largely studied. Some compounds, as LiBH_4 , store high quantities of hydrogen but desorption reaction is not completely reversible [2]. Magnesium hydride (MgH_2) theoretically store about 7.6 wt% of hydrogen and the reaction with this gas is completely reversible even after long term cycling. MgH_2 presents a high thermodynamic stability ($\Delta H \approx -75 \text{ kJ/molH}_2$) and temperature higher than 300°C are required in order to have reliable desorption kinetics [3,4]. For this reason MgH_2 is worked by mechanical treatments as ball milling or equal channel angular pressing (ECAP). By ball milling MgH_2 it is possible to create defects in the crystalline structure, to refine hydride particles reducing hydrogen diffusion path and to insert a catalyst which enhances hydrogen molecule splitting. Modifications of the microstructure due to ball milling increase hydrogen mobility and consequently allow to obtain kinetics of reaction suitable to technological applications [5–8]. A reactor for hydrogen storage is substantially a container designed to optimize heat management and gas flow through the bed of hydride. Depending on the type of material used inside the reactor, temperature and pressure have to be set to suitable values in order to allow the reactions to proceed. In the case of hydrides, absorption and desorption reactions are exothermic and endothermic respectively. Heat evolved or to be supplied during the reactions has to be managed in an optimized system otherwise kinetics could be dramatically modified [9,10].

Even if the design of the reactor allows to manage heat by cooling and heating elements, thermal conductivity is a property of the material. For this reason the design of the reactor could never be optimized if the material inserted in the reactor has not been suitably prepared.

The material mechanically treated by ball milling is in the form of powder. The use of powder in the reactors for hydrogen storage presents some problems in particular in the case of long term cycling processes. In fact the powders tend to pack and sinter during cycling and volumes of the reaction bed are not going to react with the gas because thermal conductivity and gas permeability are drastically reduced. The result is a dramatic reduction of the performances of the reactor in terms of kinetics of reaction and total hydrogen capacity [9]. Moreover problems related to particle entrainment in the gas flow could take place.

In order to avoid all the problems related to the use of powders inside the tank many efforts have been spent in preparing compacted powder systems. The powder of hydride could be mixed with other agents which enhance thermal conductivity of the powder after compaction. These agents should not react with the hydrogen storage material in the conditions of temperature and pressure of the cycling process. For this reason carbon-based materials are used as carbon nanotube, carbon nanofibers or Expanded Natural Graphite (ENG) [9–12]. Compacted powders prepared could be safely handled for example during the phase of loading of the reactor and they could be drilled to realize holes suitable for temperature measuring systems, for heat supply and dissipation lines and for gas distribution. Generally hydrides are highly affected by contamination which causes irreversible reduction of hydrogen capacity, risk of violent chemical reaction and/or flammable gas release. Some authors report that compacted powders are less affected by contaminations, in particular moisture and oxygen from air, in comparison to powders in the loose form, because of small exposed surface area and smaller gas permeability at atmospheric pressure [11].

The performances of reactors filled with compacted powder systems remain stable till they maintain this form. It has been reported that compacted powders tend to disaggregate during cycling [13–15], i.e. swelling. The swelling process is an irreversible phenomenon which starts principally with the formation of cracks and the increase of porosity which develops till complete failure of the compacted system. In order to contrast this detrimental mechanism the effect of the compaction pressure (in the range 200–600 MPa) on mechanical stability of the pellets during cycling has been studied. The authors reported that the pellets prepared even at values of compaction pressure of 600 MPa present huge dimension variations after 50 cycles [13,14].

In these conditions thermal conductivity of the pellet and gas permeability through the bed of hydride could slowly decrease resulting in the reduction of reactor performances as reported in the introduction section. The mechanism at the base of swelling has been studied but not completely understood. Nachev et al. [16] reported some in-situ dilatometry measurements and demonstrated that an irreversible phenomenon takes place during cycling. This phenomenon is described as an increase of the porosity in the system causes the failure of the pellets. In previous report the formation of cracks near ENG and larger MgH_2 particles has been reported [15]. These studies demonstrated that the mechanical stability of the pellets is a challenging goal to be achieved.

For these reasons a new procedure has been studied for the preparation of compacted powders which are more resistant to the swelling process in comparison with those prepared with classical method. The procedure is based on the deposition of a thin layer of metal on the whole pellet's surface. The quantity of metal deposited is less than 0.1% the weight of the pellet and it doesn't affect hydrogen capacity and kinetics of reaction. The variations of dimensions of the pellets after 50 cycles are 8 times smaller in comparison with the uncoated samples. Moreover this coating reduces the contact of the powder of the pellet with contaminants and consequently it makes these systems safer to be handled in not inert

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