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SIMULTANEOUS PURIFICATION AND STORAGE OF HYDROGEN

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Abstract

Specially coated magnesium particles have been shown to selectively absorb hydrogen from a hydrogen-rich gas stream such as reformate. These coated magnesium particles can store the absorbed hydrogen as required and subsequently deliver pure hydrogen, just as uncoated magnesium particles can. These coated magnesium particles could be used in a device that accepts a steady stream of reformate, as from a methane reformer, stores the selectively absorbed hydrogen indefinitely, and delivers purified hydrogen on demand.

Unfortunately, this coating (magnesium nitride) has been shown to degrade over a period of several weeks, so that the magnesium within evidences progressively lower storage capacity. We are investigating two other coatings, one of which might be applicable to hydridable metals other than magnesium, to replace magnesium nitride.

Introduction

There are several practical methods of storing pure hydrogen. Storing it by hydriding a metal is one of these methods. However, no known metal can hydride and dehydride for long when exposed to hydrogen contaminated by impurities. If the impurities are present in significant concentrations, as they are in reformate, no known metal can hydride and dehydride at all.

Likewise, there are several ways of separating hydrogen from hydrogen-rich gas mixtures like reformate. Passing it through a hydrogen-permselective membrane is one of those ways. However, hydrogen-permselective membranes are quite expensive. The thickness of these membrane is determined by a compromise: both performance and cost favor thin membranes, whereas the ability to withstand high pressure drops and the ability to use substrates with practical pore sizes both favor thick membranes.

If a particle of hydridable metal could be coated with a thin hydrogen-permselective membrane, there would be two major benefits:

1. The coated particles could accept hydrogen directly from reformate, yet could subsequently discharge pure hydrogen.
2. The membrane could be inexpensive, because a very thin membrane would suffice; a very thin membrane can be adequately supported by a solid, yet hydrogen-absorptive, metal particle.

The goal of this effort is to identify, prepare and demonstrate by testing, that magnesium powder coated with a suitable hydrogen-permselective layer will hydride/dehydride in the presence of reformate. Magnesium powder thusly coated could be termed 'reformate-tolerant magnesium' or RTM.

Why magnesium? Because magnesium hydride has the highest weight percentage hydrogen of any practical metal hydride, and because magnesium is relatively inexpensive. Another good reason is that we have already demonstrated for DOE a highly efficient means for stationary storage of hydrogen using nickel-coated magnesium powder (NCMP) and a phase change material.

Discussion

We have identified two practical uses for such reformate-tolerant magnesium:

Hydrogen Fueling Stations - A reformer-based hydrogen fueling station must include a purification device such as a pressure swing adsorber (PSA) to separate the hydrogen from the H_2O, CO_2, CO and N_2 in the reformate, plus a separate device to store the hydrogen pending demand for refueling. A single bed of reformate-tolerant magnesium powder could perform both the separation (purification) and the storage functions.

Fuel Cell Vehicles - Fuel cell vehicles utilizing on-board reformers would benefit greatly from the ability to store some of the reformate for use during startup. However, compressed gas storage of reformate is impractical, requiring both a multistage compressor and a high pressure storage cylinder. A single, small bed of reformate-tolerant magnesium powder could store enough hydrogen to run the fuel cell while the fuel processor is warming up. It could also be used to supply additional, pure, hydrogen to meet peak loads.

A suitable coating system for magnesium particles should possess the following five characteristics:

1. *Hydrogen Permselectivity* - It must pass hydrogen, but it must not pass any other species with which the magnesium might react.
2. *Chemical Inertia* - It must not itself react with the other species, lest it lose its hydrogen-permselectivity.
3. *Kinetics* - It should catalyze the dissociation of hydrogen molecules, so that the hydriding reaction kinetics are enhanced.
4. *Cost* - The coating should be inexpensive.
5. *Durability* - The coating must remain attached to the magnesium.

We recognized that a single coating might not possess all of these characteristics. We thus refer to a 'coating system,' which might consist of multiple coatings.

The major problem is that most coatings are not inert to the other species present in reformate, at least not at the temperatures (>300°C) at which magnesium hydrides/dehydrides.

Past Results

This project began with the thermal integration of nickel coated magnesium powder (NCMP) with a phase change material (PCM). This was to achieve high efficiency hydrogen storage. The mass of the NCMP and the PCM, plus the mass of the heat exchanger in which both were located, rendered this technique applicable only to stationary storage of hydrogen.

The NCMP was located on the tube side of a shell-and-tube heat exchanger, and the PCM on the shell side. As the NCMP hydrided, the heat of the hydriding reaction melted the PCM. As the NCMP dehydrided, the heat of fusion from the solidifying PCM provided the heat of the dehydriding reaction.

The primary reason for the nickel coating was to catalyze the dissociation of the H_2 molecules, so that atomic hydrogen could enter into the hydriding reaction. Nickel is also less active than magnesium, but not inactive enough to serve as a hydrogen-permselective coating.

Recent Results

Our preliminary results indicate that a coating that possesses the above characteristics may be achievable.

1. We have established that magnesium particles can easily be coated with magnesium nitride by means of chemical vapor deposition (CVD) in a fluidized bed reactor.
2. We have established that these magnesium nitride coatings do not seriously degrade the ability of the magnesium particles to hydride and dehydride in the presence of pure hydrogen.
3. We have established that these coated magnesium particles can repeatedly hydride and dehydride in the presence of a mixture of hydrogen, steam, and carbon dioxide.
4. Unfortunately, we have also established that the magnesium nitride coating does not remain hydrogen-permselective for more than several weeks.

We measured the ability of coated magnesium particles to hydride and dehydride using a closed, heated volume in which is contained the magnesium particles (with or without coatings) and a gas (either pure hydrogen or a mixture of hydrogen and other species). Our technique consists of the following steps:

1. Allow the particles and the hydrogen in the gas to reach equilibrium at 300°C ,
2. Vent some of the gas until the hydrogen partial pressure equals the hydrogen/magnesium hydride equilibrium pressure at 300°C (1.45 atm),
3. Allow the particles and the hydrogen in the gas to reach equilibrium at 350°C,
4. Allow the particles and the hydrogen in the gas to reach equilibrium at 300°C ,

Steps 3 and 4 are repeated as long as desired.

In the search for alternative coatings, we recognized that not all of the five criteria listed above are truly necessary.

- Dissociation of hydrogen molecules can be accomplished by other means, such as by mixing the coated particles with nickel powder.
- Almost any coating, if thin enough, is inexpensive (witness the use of very thin coatings of precious metals in automotive catalytic converters).

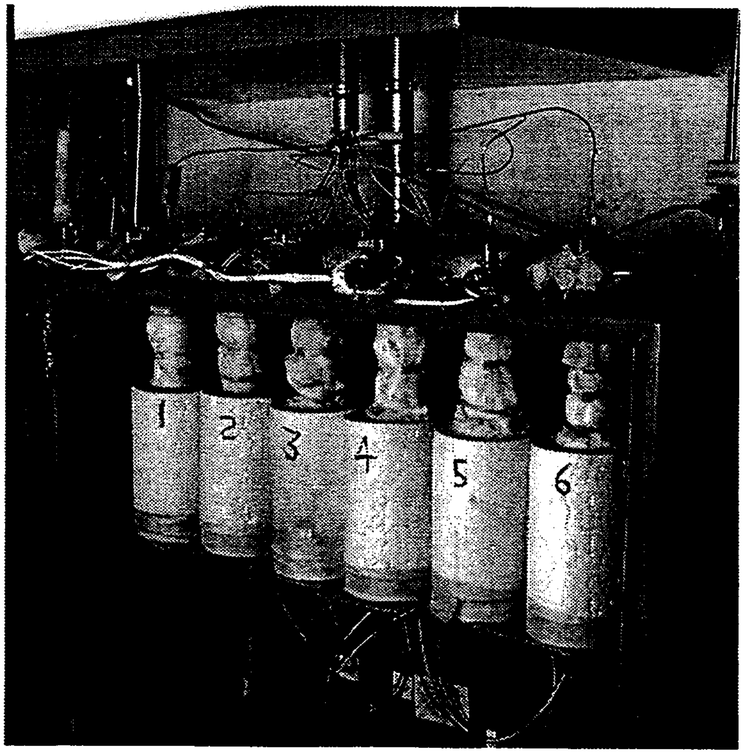
- Most coatings, if thin enough, are effectively hydrogen-permselective. This is because extremely thin coatings have imperfections, such as gap or cracks. The smallest of these cracks can pass only hydrogen. Any cracks large enough to pass other species will fill up with magnesium oxide, but this does not affect those cracks small enough to pass only hydrogen.

Therefore, perhaps we really only need a coating that

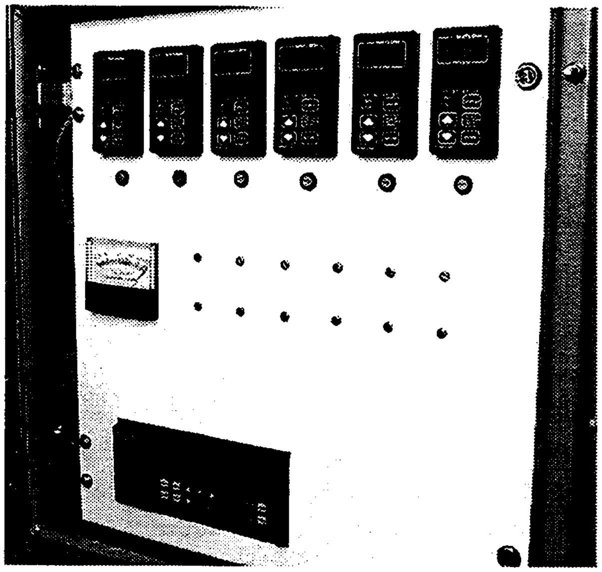
1. does not react with other species present in reformate, and
2. remains attached to the magnesium.

This theory appeared to be substantiated by the initial success of our thin coating of magnesium nitride. However, it turned out that Mg_3N_2 did, in time, react with other species present in reformate.

During the past year, we greatly improved the coated particle testing apparatus. No longer is it necessary to coat and test the particles in the same reactor. Now it is possible to coat particles in the original reactor, and to test six separate samples of coated particles simultaneously in six separate test sections, shown below.



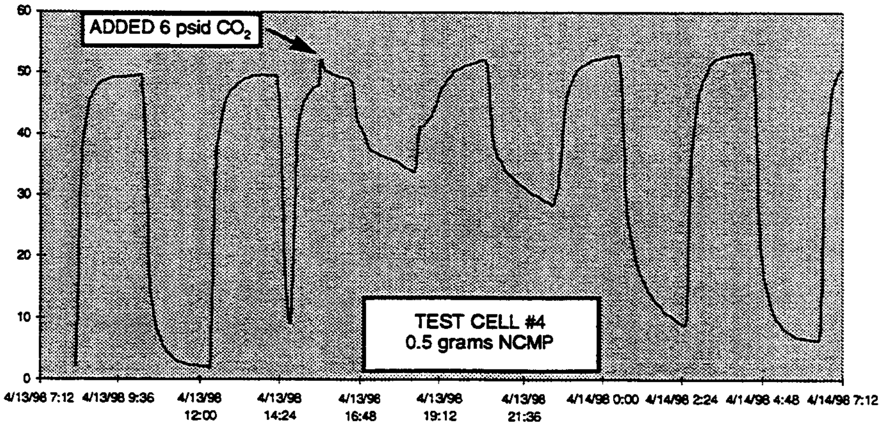
Each of these test sections has its own electric heater, controlled by its own programmable controller. The temperatures and pressures within all six test sections are monitored by thermocouples and pressure transducers, all connected to a datalogger, shown below.



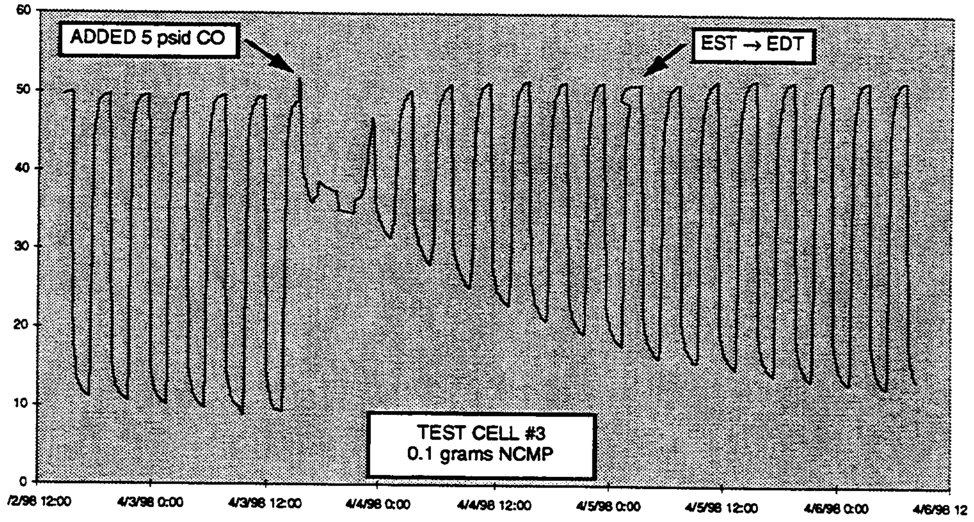
It is possible to retrieve the data from that datalogger remotely, using a pair of modems.

We used this improved facility to determine the sensitivity of NCMP to CO_2, H_2O and CO, individually and simultaneously. This showed that NCMP is inert to neither CO_2, H_2O nor CO.

Interestingly, NCMP can recover from exposure to a fixed amount of CO, as shown below



It can also recover from exposure to a fixed amount of CO_2, as shown below



However, neither of these results should be taken to suggest that NCMP could withstand exposure to a continued supply of either CO or CO_2, as it would be if exposed to a reformate stream.

Future Work

We have identified two new potential coatings for magnesium, and plan to evaluate them. One of these coatings is a salt of magnesium, so it presumably would be firmly attached to the magnesium powder. The other of these coatings would appear to have all of the other required attributes.

We have embarked on a literature search to investigate the fabricability and the thermochemical stability of the first of these coatings.

We have also contracted to have a sample of the second coating prepared, so that we can test its ability to hydride/dehydride. We will first test this coated powder in pure hydrogen, and then in mixtures of H_2, CO, CO_2 and H_2O.

We also plan to investigate means by which the instability of Mg_3N_2 might be accommodated. For example, how realistic might it be to re-coat the particles periodically? Or, might NH_3 in reformate prevent decomposition of Mg_3N_2?