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HYDROGEN STORAGE IN FULLERENES AND LIQUID ORGANIC HYDRIDES

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Abstract

A major effort was made during the current year to bring to a more practical level the hydrogenation/dehydrogenation conditions using fullerenes and some liquid organic hydrides. Based on the idea that improving effective contact between a solid hydrogen storage material and the catalyst may reduce the relevant process activation energies, three separate but related techniques were attempted for fullerenes: (1) using liquid catalysts, (2) doping fullerenes with alkali ions, and (3) dissolving fullerenes and their hydrides in selected low-temperature molten salts. In all three cases, it was found that significant hydrogenation can be achieved below 200°C and dehydrogenation around 200°C. The hydrogen pressure needed for hydrogenation can be as low as several hundred psi. Some cyclical hydrogenation/dehydrogenation tests on the same sample were also performed. The hydrogenation/dehydrogenation tests on a related organic hydride (as an alternative hydrogen storage system) reported last year were expanded using various catalysts. Metallized membranes capable of separating the released hydrogen from the organic hydride with near 100% efficiency were utilized and gravimetric capacities around 6% were obtained.

Introduction

Fullerenes or mixed fullerenes (MF) and some related organic hydrides can absorb up to 7 wt%

of hydrogen and release it under suitable conditions. For example, there is 7.7 wt% of hydrogen stored in $C_{60}H_{60,}$ and our experimental results have already indicated a 6 wt% hydrogen storage feasibility in fullerenes (corresponding to $C_{60}H_{48}$) and about 7 wt% in a related organic hydride. In order to develop a practical hydrogen storage system using these materials, Oak Ridge National Laboratory (ORNL) and Materials & Electrochemical Research (MER) Corporation have been engaged in a joint effort through a Cooperative Research and Development Agreement (CRADA) to (1) understand the mechanism of hydrogen storage in fullerenes and some organic hydrides, (2) optimize the hydrogen absorption/desorption properties of these materials, (3) develop the thermal management technology needed for hydrogen storage device designs, and (4) construct and demonstrate experimental hydrogen storage devices using these materials.

Through the analysis of hydrogenation/dehydrogenation data, physical model development, and thermophysical property measurements, we have demonstrated that the hydrogen storage processes in the materials are thermally activated and involve sizable activation energies and heats of hydrogenation (Wang *et al*. 1995, Wang *et al*. 1996, Murphy *et al*. 1997, Wang *et al*. 1998, Loutfy *et al*. 1998). We have found that the activation energies are highly dependent on the catalysts used and can be tailored to yield practical hydrogen storage conditions including hydrogenation/dehydrogenation pressure and temperature. The thermally activated processes, together with the sizable heat of hydrogenation, point to the need for and importance of thermal management. The approach adopted in the present project is to continue to develop and improve catalysts, to better understand the physics involved, and to develop thermal management techniques to achieve efficient storage operations.

Past Results

The beginning effort on this project emphasized the use of simple physical models to interpret limited experimental data related to the hydrogenation and dehydrogenation of fullerene samples (Wang *et al*. 1996). It was found that representations based on thermal activation mechanisms provided reasonable characterizations of both the absorption and desorption measurements. Subsequent combustion calorimetry measurements provided preliminary substantiation of the earlier estimates from the absorption/desorption data (Murphy *et al*. 1997). The results were employed to develop an integrated model to guide materials development and to simulate thermal management of some simplified storage devices using a commercial code based on finite control volume methods. It has been demonstrated that lowering the activation energies for hydrogenation/dehydrogenation is most important in materials development and that thermal management is very relevant in the performance of a storage device (Murphy *et al*. 1997). Tests employing various catalysts were conducted for fullerenes in the solid phase, but they yielded only limited decreases in activation energies. However, initial tests employing both a catalyst and a solvent of fullerenes showed promising results, suggesting that close contact between the catalyst and solid phase fullerenes may be important.

During the last review period, progress was made in two main areas: the data base for the effects of combining solvent and catalyst on the absorption/desorption of hydrogen in fullerenes was expanded, and the hydrogenation/dehydrogenation of a related organic hydride (as an alternative hydrogen storage system) was explored (Wang *et al*. 1998, Loutfy *et al*. 1998). In the first area, experiments with fullerenes in a solvent showed that more than 6 wt% of hydrogen can be charged at 180°C, 350B400 psi. In addition, dehydrogenation of fullerene hydrides below 225°C was demonstrated using a solvent and an Ir-based P-C-P pincer complex catalyst developed by the University of Hawaii. In the second area, multi-cycle tests involving the hydrogenation/dehydrogenation of an organic hydride showed a hydrogen storage capacity of 7 wt%. The resulting data were analyzed and interpreted to elucidate relevant trends and mechanisms. It was demonstrated that the storage processes in the organic hydride are similar to those in the fullerenes, but with much smaller activation energies and heat of hydrogenation.

Current Year Results

A major effort was made during the current year to bring the hydrogenation/dehydrogenation conditions to a more practical level. Based on our past experience, conceptual analysis, and model development, initiatives were undertaken to improve effective contact between fullerenes and other materials that might substantially reduce the relevant process activation energies. Three separate but related techniques were attempted: (1) using liquid catalysts, (2) doping fullerenes with alkali ions, and (3) dissolving fullerenes and their hydrides in selected low-temperature molten salts. In some cases, cyclical hydrogenation/dehydrogenation tests on the same sample were performed.

Some cyclical hydrogenation/dehydrogenation test results (up to 11 cycles) of a liquid organic hydride were reported in the previous DOE Hydrogen Program Review Meeting (Wang *et al*. 1998). These tests were extended using various catalysts to evaluate their performance. Metallized membranes capable of separating the released hydrogen from the organic hydride near 100% efficiency were developed. Gravimetric capacities around 6% were obtained. The approach to full capacity was found to be limited by kinetics as reactant concentrations decreased.

Thus, during the review period, four distinct novel approaches were tested and analyzed for their hydrogenation/dehydrogenation potentials. The associated results are described in the remainder of this paper.

Hydrogenation/Dehydrogenation of MF Using Liquid Catalysts

A family of liquid catalysts was prepared and many hydrogenation/dehydrogenation experiments were performed to evaluate promising catalysts. In these experiments, fullerenes or MFs were soaked in a liquid catalyst (without solvent). Hydrogenation was achieved by heating the samples under elevated hydrogen pressures and dehydrogenation was achieved by heating the hydrides at relatively low hydrogen pressures. The results indicated that these liquid catalysts can significantly ease the hydrogenation and dehydrogenation conditions reported previously (Wang *et al*. 1998, Loutfy *et al*. 1998).

Hydrogenation

Figure 1 shows the hydrogenation results of a dehydrogenated $C_{60}H_{36}$ sample as an example. The liquid catalyst used in this case was a Ti-complex. As can be seen from the figure, effective hydrogenation started around 120°C. The hydrogen pressure used in this experiment was about 400**S**500 psi (27**S**34 atm).

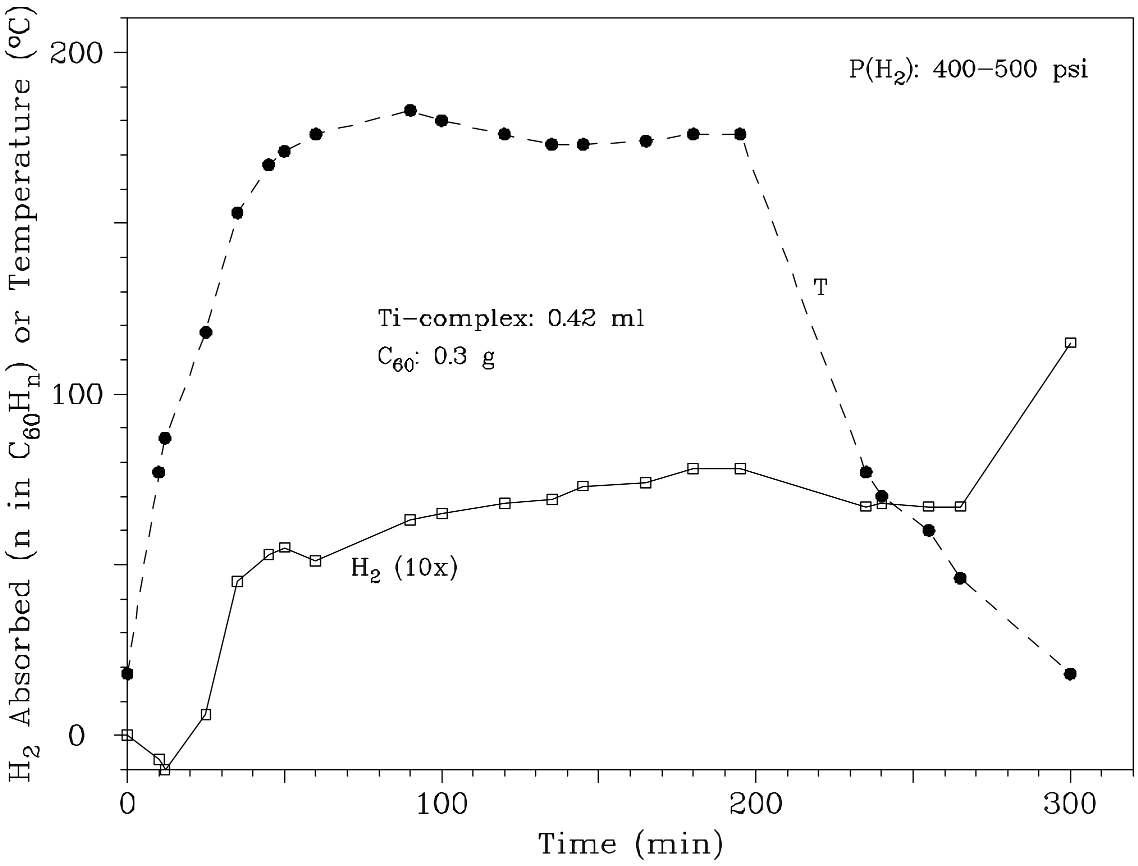

Figure 1 - Hydrogenation of a dehydrogenated $C_{60}H_{36}$ sample using a liquid Ti-complex as catalyst.

Dehydrogenation

In the dehydrogenation experiments, fullerene or MF hydrides were combined with a liquid catalyst (such as a Zr-complex or a Ti-complex) and heated to some moderate temperature to release the hydrogen. A preliminary result using a Zr-complex as catalyst is shown in Fig. 2 as an example. The figure suggests that the catalyst was very effective for the dehydrogenation of fullerene hydrides. Note, however, that only about 50% of the hydrogen was released in this experiment. There was some indication that the liquid catalyst reacted with the hydrogen released and became solidified. As a result, the catalyst may have lost some of its capability during the dehydrogenation process. Through careful analysis and experimental testing, the optimal temperature/pressure regimes for hydrogenation and dehydrogenation using this type of catalysts were established.

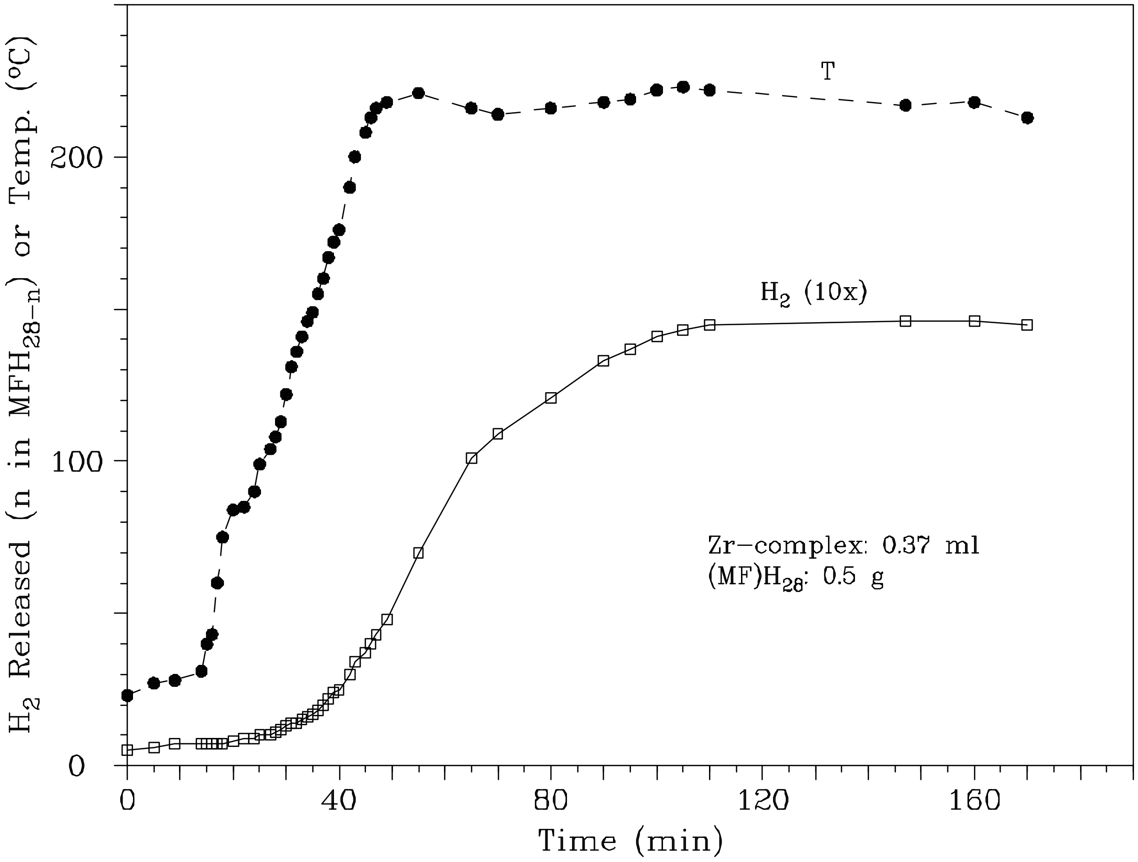

Figure 2 - Dehydrogenation of a $(MF)H_{28}$ sample using a liquid Zr-complex as catalyst.

Cyclical Test

Figure 3 shows the cyclical hydrogenation/dehydrogenation results of a MF hydride sample. The starting material was 0.2 g of $(MF)H_{36}$. The liquid catalyst used in this case was 0.3 ml of a Zr-complex. In the figure, the hydrogenation and dehydrogenation portions of each cycle are labeled as Hy and DeHy, respectively. The Hy and DeHy half-cycles were plotted together along a continuous time-coordinate. This is for illustration purpose only; the actual experiments for the half-cycles were performed separately on the same sample at different times. As can be seen from the figure, using this Zr-complex as liquid catalyst, hydrogenation can be achieved near 150°C and dehydrogenation around 200°C. The hydrogenation pressure used in these experiments was about 525**S**700 psi (36**S**48 atm). Note that in the figure, scc stands for standard cubic centimeter. One mole of an ideal gas at standard conditions has a volume of 22,400 scc.

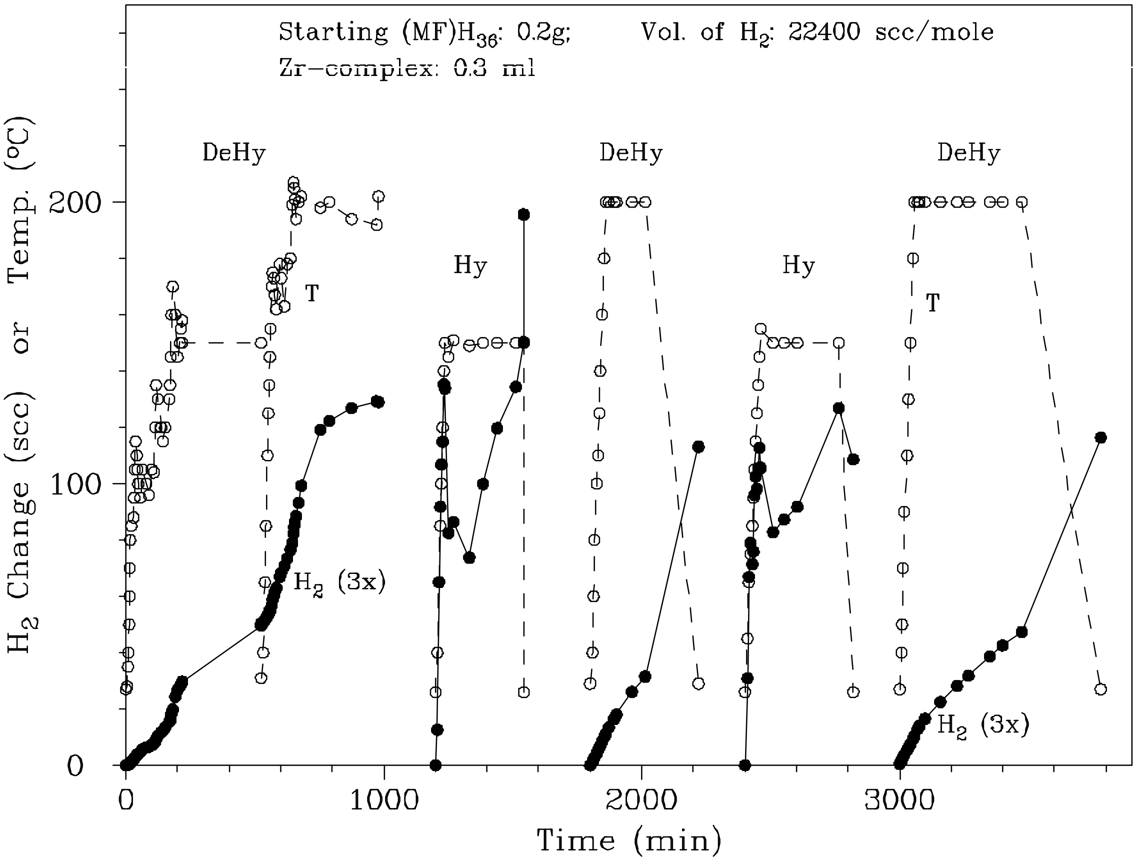

Figure 3 - Cyclical Hydrogenation (Hy) and Dehydrogenation (DeHy) of a $(MF)H_{36}$ sample using a liquid Zr-complex as catalyst.

Hydrogenation/Dehydrogenation of MF Doped with Alkali Ions

The idea of doping fullerenes with selected alkali ions (3 per MF) was to determine whether the ions could modify the electronic properties of the fullerene structure so as to effectively weaken the hydrogen bonds and, thereby, to ease the conditions for the hydrogenation/dehydrogenation cycle. Our results indicated that significant amounts of hydrogen can be added to and taken out of the doped fullerenes under moderate conditions.

Hydrogenation

Figure 4 shows the hydrogenation results of a $(MF)(Alk)_3$ sample, where (Alk) stands for the alkali ions in the doped material. During this experiment, the material was exposed to an elevated hydrogen pressure (1050**S**1470 psi) in a sealed chamber and was heated up to and maintained at 200°C for six hours, and then was left to cool down to room temperature. No catalyst was used in this hydrogen storage system. As can be seen from the figure, the absorption started from near room temperature. This seems to be somewhat different from the hydrogenation results of fullerenes without alkali ions.

As can be seen from Fig. 4, the absorption was still going on at the end of the heating period (T = 200°C). The maximum amount of hydrogen absorbed in this experiment was estimated to be 35 H:s per MF. It is known that significant amounts of hydrogen can exist in alkali-ion intercalated graphite compounds. It is not clear whether that is relevant to the hydrogenation of doped fullerene materials. More experiments are needed to explore the physics of the hydrogenation process of $(MF)(Alk)_3$.

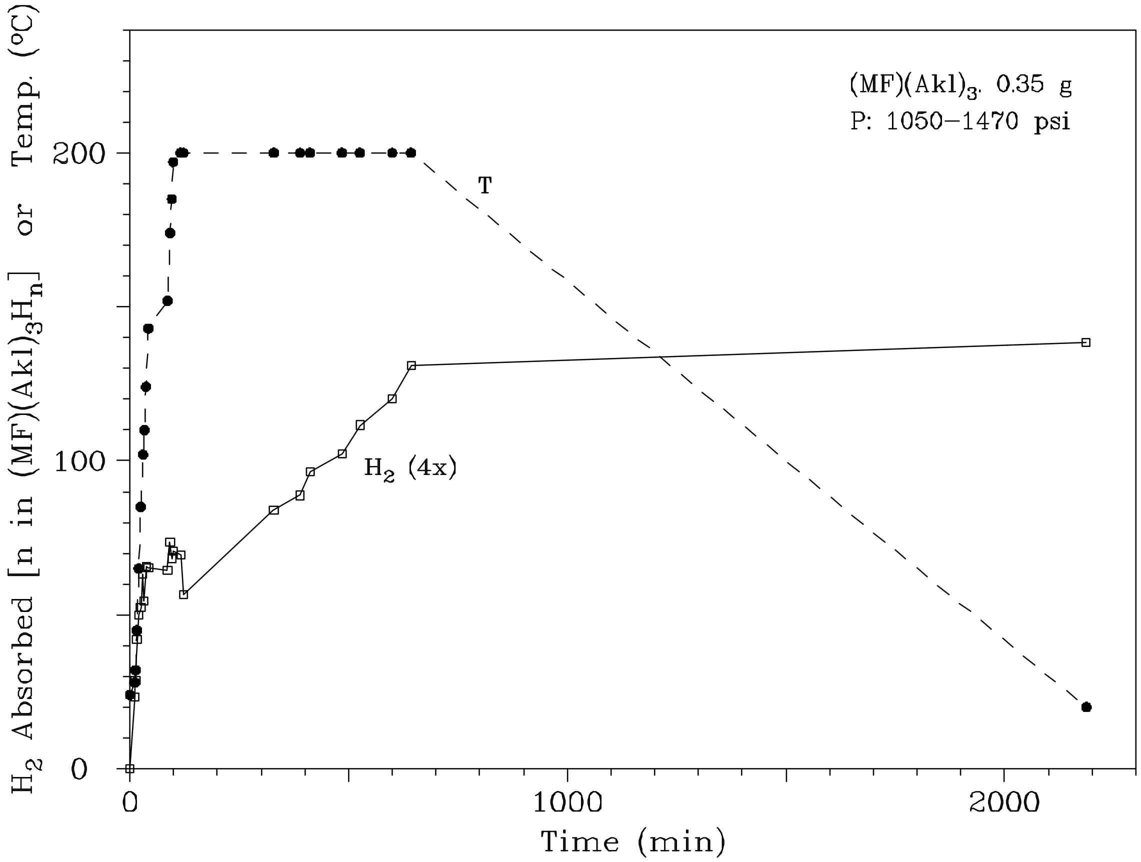

Figure 4 - Hydrogenation of an alkali-ion doped MF sample.

Dehydrogenation

Figure 5 shows the dehydrogenation results of the $(MF)(Alk)_3$ sample that was hydrogenated with about 35 H:s per MF (see Fig. 4). The shape of the dehydrogenation curve indicates the trend of a thermally-activated process: rapid release of hydrogen begins only after the temperature becomes high enough (e.g., around 100°C in the Fig. 5). The gradual decrease in the dehydrogenation rate during the period at T = 200°C was probably due to the gradual depletion of hydrogen in the sample. As can be seen from the figure, as the sample cooled down to the room temperature, the amount of released hydrogen actually decreased from its maximum value. This was probably due to the re-absorption of some of the released hydrogen as hydrogenation can happen near room temperature (see Fig. 4). According Fig. 5, the maximum amount of hydrogen released during this experiment was about 10 H_2s per MF.

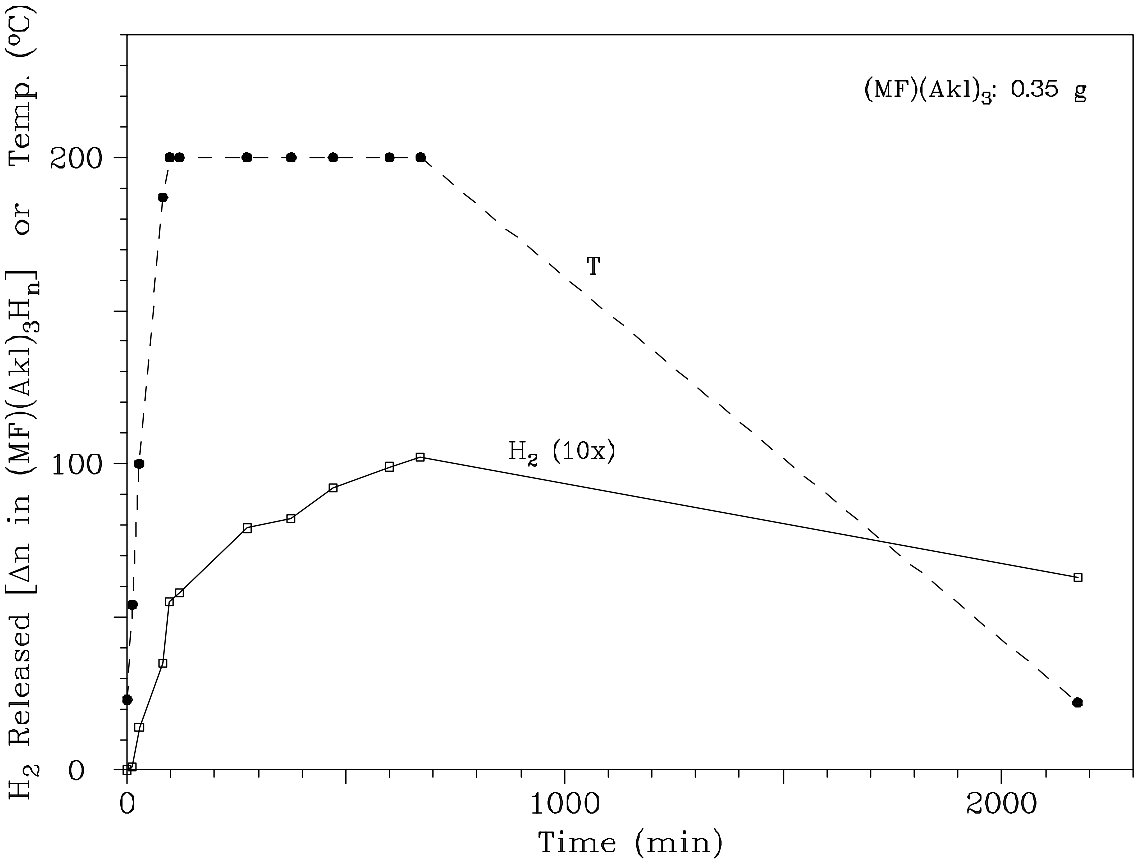

Figure 5 - Dehydrogenation of a hydrogenated alkali-ion doped MF sample.

Hydrogenation/Dehydrogenation of MF in Molten Salts

The third technique used to improve effective contact between fullerenes and other materials to reduce activation energies involved using low temperature molten salts to disperse catalysts and fullerenes. These molten salts have a variety of melting points and low vapor pressures at moderate temperatures. Our experimental results indicated that significant amounts of hydrogen can also be added to and taken out of the dispersed systems under moderate conditions.

Hydrogenation

Figure 6 shows the hydrogenation results of a MF sample in a selected molten salt containing Sn with a selected catalyst compound containing Pt as an example. As can be seen from the figure, effective hydrogenation can be achieved around 170°C. The hydrogen pressure used in this experiment was about 470S630 psi (32S43 atm). The amount of hydrogen absorbed at the end of heating was about 18 H:s per MF.

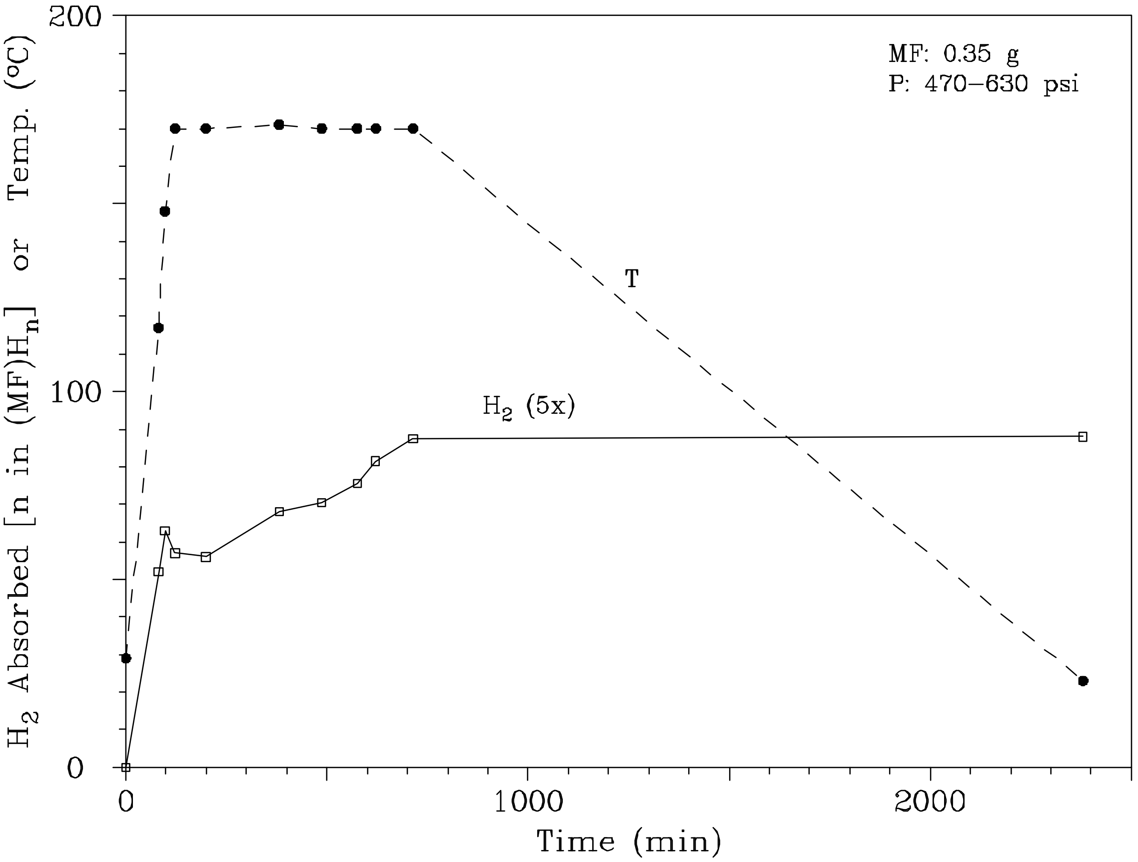

Figure 6 - Hydrogenation of an MF sample in a molten salt.

Dehydrogenation

Figure 7 shows the dehydrogenation results of the MF sample that was hydrogenated in a molten salt (see Fig. 6). According to Fig. 7, the maximum amount of hydrogen released during this experiment was about 5.5 H:s per MF.

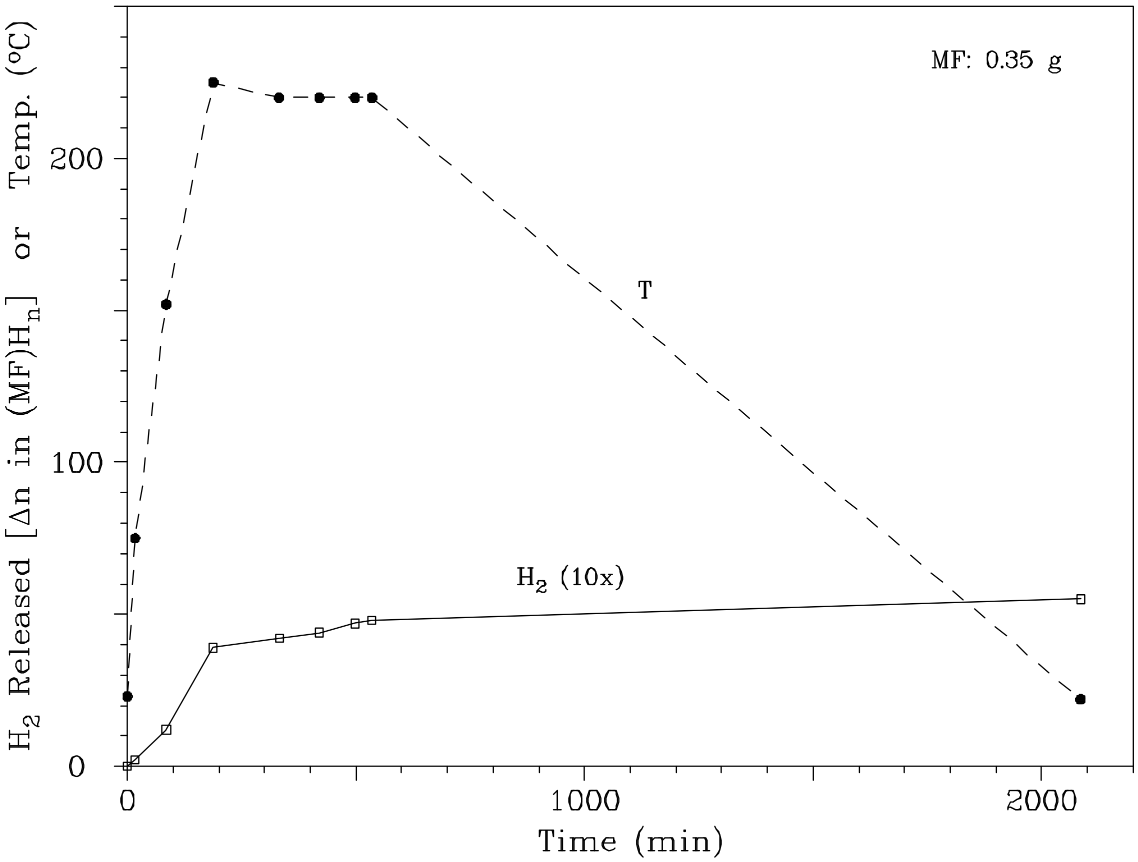

Figure 7 - Dehydrogenation of a hydrogenated MF sample in a molten salt.

Cyclical Hydrogenation/Dehydrogenation of Organic Hydrides

As reported last year, the hydrogenation/dehydrogenation of a liquid organic hydride (as an alternative hydrogen storage system) was explored and multi-cycle tests yielded very promising results (Wang *et al*. 1998). During the current year, additional tests were made to study various catalysts and to develop metallized membranes to separate the released hydrogen from the liquid hydrides. Figures 8 and 9 show the hydrogenation of a liquid organic hydride and the dehydrogenation of the hydrogenated liquid hydride, respectively. In each case, 100 ml of storage material was used but the amount of hydrogen absorbed or released was several hundred times this volume. At this time about 80% conversion can be achieved (about 6 wt%) using a new catalyst dispersion method and a newly developed metallized membrane as hydrogen filter. The approach to the full theoretical capacity of more than 7 wt% is limited by slow kinetics at low hydrogen content near the end of dehydrogenation. Improved catalytic configurations and thermal management may further reduce the limitation.

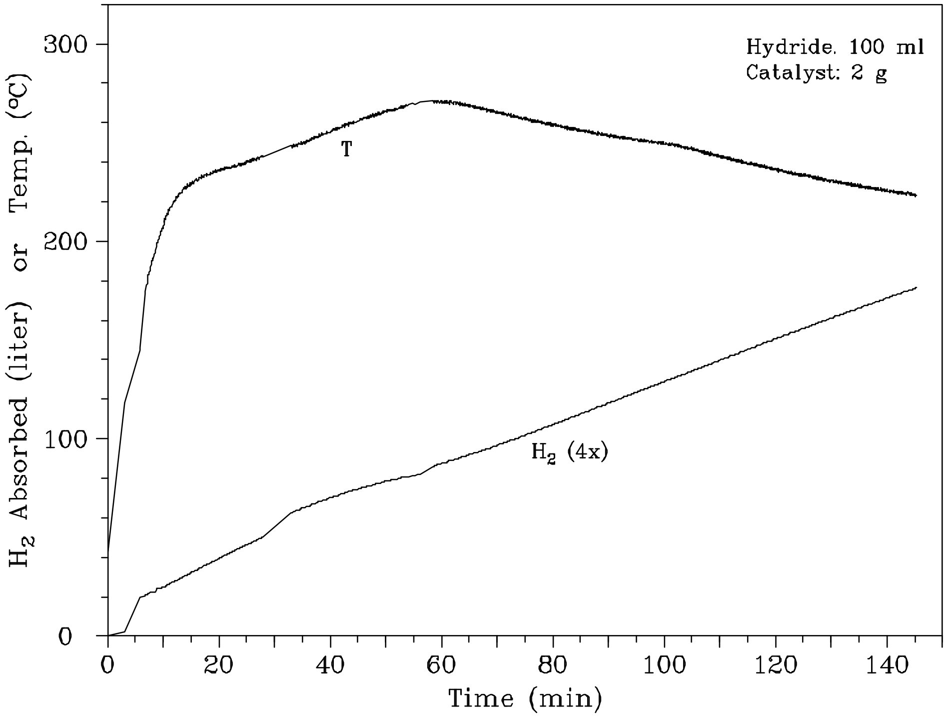

Figure 8 - Hydrogenation of a liquid organic hydride sample.

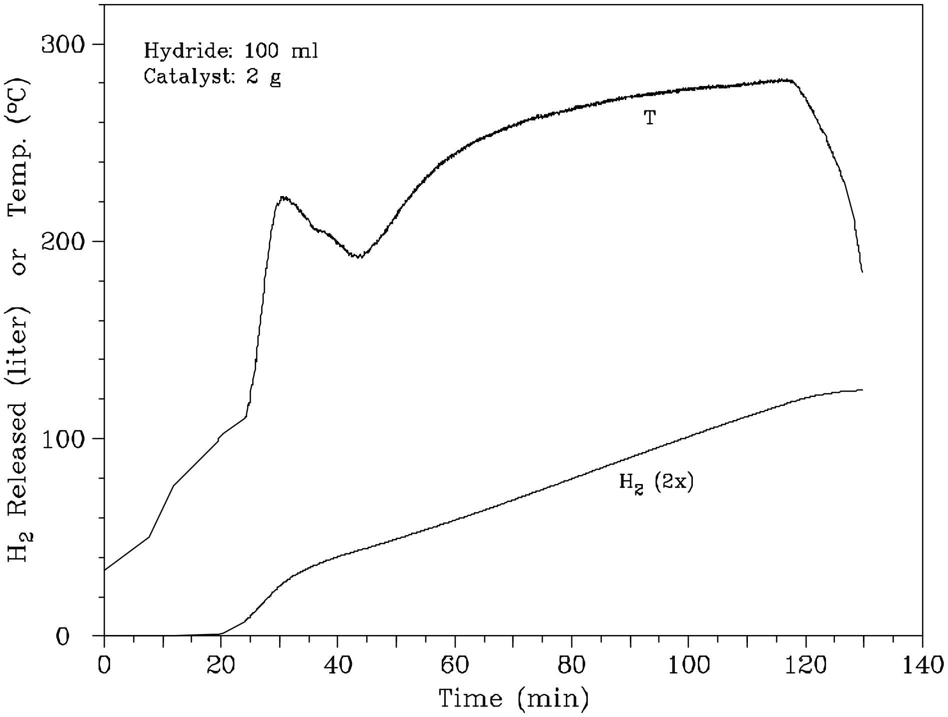

Figure 9 - Dehydrogenation of a hydrogenated liquid hydride sample.

The performance of the liquid organic hydride mentioned above can be summarized as follows:

High gravimetric density:	$\geq$ 6 wt%
High volumetric density:	65 kg/m^3
High rate of hydrogen release	6 liter H_2/min/liter of organic hydride
Reversible	
Low cost	Commercially available
Insensitive to contaminates	
Relatively low heat of hydrogenation	Less than that of fullerenes
Ready for demonstration	

In summary, both the fullerenes and the organic hydride studied in the project have been demonstrated to be promising hydrogen storage materials with up to 7 wt% potential capacities.

Plans for Future Work

A substantial portion of the methodology developed and the experience gained in the project can be applied to both fullerenes and the liquid organic hydrides studied. We plan to

1) investigate the achievable improvements using liquid catalysts, alkali ion doping, and molten salts with fullerenes,
2) expand the data base for the liquid organic hydride hydrogenation/dehydrogenation option,
3) extend the heat of dehydrogenation measurements,
4) employ characteristics of the most attractive options to create relevant models and simulations of practical hydrogen storage units, and
5) explore the potential of other novel systems for hydrogen storage.

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