

FEASIBILITY OF FULLERENE HYDRIDE AS A HIGH CAPACITY HYDROGEN STORAGE MATERIAL

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Abstract

The results of recent investigation of fullerene–fullerene hydride system as a potential high capacity hydrogen storage option are presented. Theoretically, C_{60} fullerenes can reversibly store up to 7.7 wt.% hydrogen by forming fullerene hydride $C_{60}H_x$. However, high temperature and pressure are currently required to enable hydrogen exchange in this system. For example, direct hydrogenation of fullerenes in the presence of gaseous hydrogen at $\sim 450^\circ\text{C}$ and ~ 3 MPa yields fullerene hydride with ~ 6.1 wt.% hydrogen content. Over the past years, MER has been searching for practical ways to facilitate hydrogen storage on fullerenes at milder conditions. The main focus of the research was concentrated on optimizing catalytic system including transition-metal liquid state catalysts, as well as modifying electronic structure of fullerenes by doping them with electron-donating elements (for example, alkali metals). As a result of this investigation, certain progress was made in lowering the temperature and pressure required for hydrogenation. However, dehydrogenation parameters still remain to be optimized.

Introduction

Hydrogen is a convenient, safe, versatile fuel source that easily converts to a desired form of energy, without releasing harmful emissions. One of the major applications of hydrogen as a fuel source is for the fuel cell-based energy sources, both for military and commercial use due to recent developmental advances in fuel cell technology. Currently, there are four major approaches

to hydrogen storage. They include physical storage via compression or liquefaction; chemical storage in hydrogen carriers (e.g. methanol, ammonia); metal hydrides; and gas-on-solid adsorption (physical and chemical). Although each storage method possesses desirable attributes, no approach satisfies all of the efficiency, size, weight, cost and safety requirements for transportation or utility use.

Among other options, carbon-based hydrogen adsorption materials hold particular promise for meeting and exceeding the hydrogen storage energy density targets.

Fullerenes, a new form of carbon with a closed-caged molecular structure first detected by Smalley [Kroto and Smalley, 1985], were selected for investigating as a potential hydrogen storage material based on their ability to react with hydrogen via hydrogenation of carbon-carbon double bonds. The theory predicts that maximum of 60 hydrogen atoms can be attached both to the inside (endohedrally) and outside (exohedrally) of the fullerene spherical surface and that a stable $C_{60}H_{60}$ isomer can be formed loaded with ~7.7 wt.% hydrogen. Since many of the fullerene reactions appear to be reversible, if a 100% conversion of $C_{60}H_{60}$ is achieved, 30 moles of H_2 gas would be liberated from each mole of fullerene hydride:



Since 1 mole of H_2 gas can produce 67.25 W·hr of electric power, 30 moles of H_2 generated by 1 mole of $C_{60}H_{60}$ should produce 2017.5 W·hr of electricity resulting in 2.6 kW·hr/kg or 4.4 MWh/m³ power density (density of $C_{60}H_{60}$ is ~1700 kg/m³).

During our previous studies, it was shown that thermodynamically both hydrogenation and dehydrogenation reactions can occur at moderate conditions, however, practical realization poses a real challenge.

This paper summarizes and discusses results of the past year research activities aimed at optimization of hydrogenation and dehydrogenation reactions in fullerene-fullerene hydride system with the objective of increasing the weight percentage of reversible hydrogen at mild reaction conditions.

Background

The process of hydrogenation of fullerenes involves formation of C-H bonds as a result of breakage of C=C double bonds of fullerenes and H-H bonds of molecular hydrogen to form hydrogen atoms. Although the hydrogenation reaction is exothermic (the heat is released as a result of reaction), additional energy is required to break these bonds. Besides the thermodynamics involved into this process, a certain energy barrier has to be overcome for the reaction to occur. From our experimental results of solid state hydrogenation of fullerenes in gaseous hydrogen atmosphere at temperature ranging between 400 – 450°C and pressure ranging between 60 – 80 MPa, the activation energy for the hydrogenation was estimated to be 100 kJ/mole (1.0 eV/ H_2). Considering the dehydrogenation process, the potential barrier, associated with the breakage of C-H bonds, re-establishing C=C double bonds and forming molecular hydrogen, is even higher - about 160 kJ/mole (1.6 eV/ H_2). The conceptual model for hydrogenation and dehydrogenation is schematically illustrated in Fig. 1.

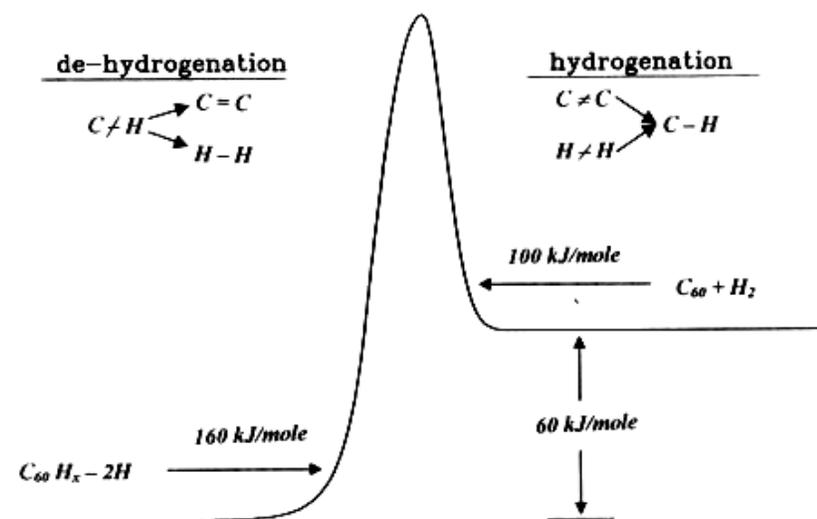


Figure 1. Activation Energy of $C_{60}H_x \rightleftharpoons C_{60}$ Transformation

Typically, high reaction temperature and pressure are required to overcome these barriers. That is why selection of the proper catalyst is crucial for facilitating the reactions at milder conditions.

During the course of investigation, MER has explored various options to improve reversible hydrogen storage on fullerenes under moderate reaction conditions including a number of novel approaches, such as using liquid catalysts, molten salts, changing electronic structure of fullerenes, etc. As a result, significant progress was made in carrying out hydrogenation and dehydrogenation reactions at temperatures below 200°C and moderate pressures. Although the percentage of reversibly exchangeable hydrogen in these systems still remains below the level required for efficient practical applications, the conducted research has produced an invaluable amount of unique knowledge and resulted in better understanding of the processes and mechanisms involved in hydrogen related-chemistry of fullerenes.

This paper discusses the most interesting results, both theoretical and experimental, obtained during the course of the investigation, which create the basis for further research aimed at more complete realization of the hydrogen storage potential offered by fullerenes.

Technical Approach and Summary of Past Work

MER has been investigating hydrogenation of fullerenes for nearly a decade. The motivation was based on the theoretical capacity of $C_{60}H_{60}$ hydride to store ~7.7 wt.% hydrogen. Initial attempts to produce hydrogenated fullerenes by direct hydrogenation in gaseous hydrogen atmosphere at elevated temperature and pressure (400 – 450°C, 60 – 80 MPa) resulted in $C_{60}H_x$ compounds with hydrogen content up to 6.1 wt.% (Fig. 2).

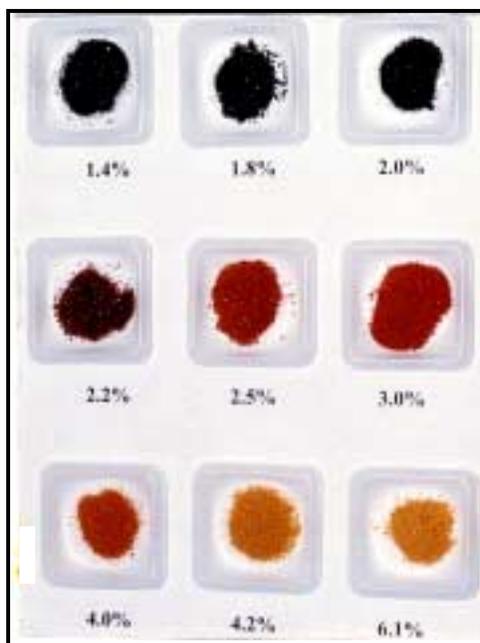


Figure 2. Samples of hydrogenated fullerenes

Introduction of the catalyst (supported precious metals, for example, Pt/C) allowed us to somewhat decrease the temperature and pressure required for the reaction, although not significantly due to insufficient contact area between the two solids. Further introduction of the liquid phase in the form of a solvent resulted in a dramatic decrease in temperature and pressure of hydrogenation (180°C and 12 MPa). However, the weight percentage of stored hydrogen also dropped due to the additional weight of the solvent.

These results confirmed the later findings based on thermodynamical analysis conducted on hydrogen storage in fullerenes [Loutfy, 2001], which suggested that both reactions of hydrogenation of fullerenes and dehydrogenation of fullerene hydrides are thermodynamically favorable at reasonably low temperatures; it is just a matter of overcoming corresponding energy barriers. Also, the analytic results showed that in order to increase the amount of reversible hydrogen, fullerenes shall be hydrogenated to as high levels as possible (practically 6% or better) because of varying stability of fullerene hydrides ($C_{60}H_{36}$ appears to be the most stable form of fullerene hydrides since it has the lowest enthalpy of formation).

Thus, in order to lower the activation energy responsible for high temperature and pressure conditions of the reactions involved in hydrogen storage on fullerenes, the following approaches should be considered:

- Selecting and optimizing the catalytic system,
- Conducting reactions in the liquid phase,
- Modifying the electronic structure of fullerenes.

Experimental Results and Discussion

In order to realize the approaches listed above, the enhancement of fullerene-based hydrogen storage systems were studied using liquid phase transition metal catalysts which would provide catalytic activity along with liquid phase for the reaction, and fullerene doping with alkali metals to facilitate charge transfer by modifying their electronic structure.

Liquid Phase Catalytic System

The following transition metal-based liquid state catalysts were used for evaluation: $\text{Ti}(\text{OPr}^i)_4$, $\text{Ti}(\text{O}i\text{Bu})_4$, $\text{Zr}(\text{O}i\text{Bu})_4$, $\text{VO}(\text{OC}_3\text{H}_7)$, $\text{Ta}(\text{OC}_2\text{H}_5)_5$, and $\text{Nb}(\text{OC}_2\text{H}_5)_5$. Implementation of these catalytic materials enables a liquid-state introduction of Ti, Zr, V, Nb, Ta ions to the fullerene solid, resulting in promoting fullerene hydrogenation and dehydrogenation due to a much higher contact surface area. Similar materials, namely $\text{Ti}(\text{O}i\text{Bu})_4$ were also reported to be capable of catalyzing the reaction of dehydrogenation of NaAlH_4 and Na_3AlH_6 [Jensen, 1999].

As a result of conducting a series of experiments, it was shown that reversible hydrogenation of fullerenes and dehydrogenation of fullerene hydrides can be achieved in the temperature range of 180–250°C in the presence of liquid transition metal catalysts. However, the amount of rechargeable hydrogen was still too low. Figure 3 illustrates the results of dehydrogenation run performed using fullerene hydride C_{60}H_x ($x \approx 28$) mixed with $\text{Ti}(\text{OPr}^i)_4$ at 250°C.

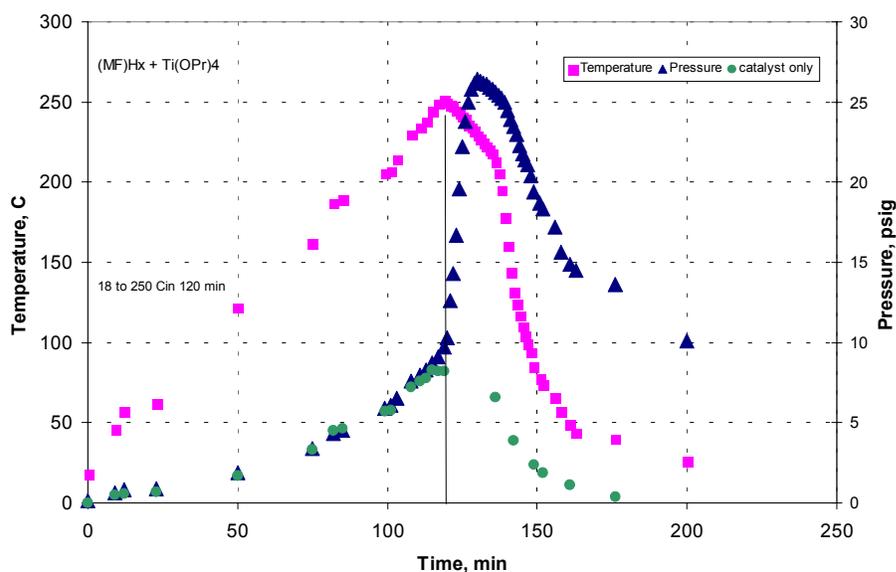


Figure 3. Dehydrogenation of C_{60}H_x in presence of $\text{Ti}(\text{OPr}^i)_4$

The data presented on the graph show the change in pressure in the reactor containing fullerene hydride mixed with the catalyst versus time as the temperature reaches 250°C and then drops. For comparison purposes, similar data obtained for the catalyst only are plotted. As one can see from the graph, the pressure in the reactor increases with temperature up to ~27 psi in case of C_{60}H_x + catalyst, as opposed to only ~8 psi in case of catalyst alone. When the system was cooled down,

the residual pressure in the reactor with fullerene hydride was ~ 0 psi, which was first interpreted as caused by evolved hydrogen. However, the gas chromatography analysis of the gas phase in question revealed only $\sim .5\%$ of hydrogen present in the gas mixture with, the rest of it being saturated hydrocarbons. In addition, when the reactor was opened, it appeared that the initial slurry composed of fullerene hydride and liquid catalyst was converted to a solid compound. This suggests that fullerene hydrides actually react with $\text{Ti}(\text{OPr}^i)_4$ causing this conversion. Similar results were obtained with other catalysts. In fact, rest of the catalysts appeared to be even less thermally stable than $\text{Ti}(\text{OPr}^i)_4$. The effect of heating on catalyst conversion in the presence of pressurized hydrogen gas can be clearly seen from the data presented in Table 1.

Table 1. State change of the liquid metal alkoxide catalysts as a function of temperature and hydrogen pressure

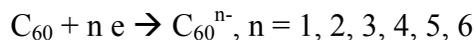
Catalyst	RT \rightarrow 150°C Vacuum	RT \rightarrow 200°C 18-25 psi, 6 h	150°C 500-550 psi, 6 h	200°C 500-550 psi, 6 h
$\text{Ti}(\text{OPr}^i)_4$	Liquid	Liquid	Liquid	Slurry
$\text{Zr}(\text{O}i\text{Bu})_4$	Liquid	Liquid	Slurry	White solid
$\text{VO}(\text{OPr}^i)_3$	Liquid (turned purple)	Suspension (purple)	Dark solid	N/a

As it can be seen from the Table 1, the catalysts survive the temperature of 200°C at low hydrogen pressure, but start converting to a solid under higher pressure. As a result, maximum hydrogen discharge can be obtained only during the first run, when the liquid phase is still present. When attempting repeated cycling, performance declines due to loss of the liquid phase in the process of hydrogenation, when elevated hydrogen pressure is required.

Hence, transition metal-based liquid catalysts do enhance hydrogen exchange in fullerene–fullerene hydride system, but the benefit is insufficient due to their limited stability and added weight.

Modifying Electronic Structure of Fullerenes

Another approach utilized in this work was based on changing the electronic structure of fullerenes by doping with alkali metals (Na, K, Li). When reacting with fullerenes, alkali metals donate their electrons to fullerenes causing charge transfer and resulting in formation of *fulleride anions* [Goldshleger, 1997; Cioslowski, 1995]:



The process of intercalation was conducted by placing weighed stoichiometric amounts of fullerene powder and alkali metal (Na, K, Li) into a closed container, heating to 400°C for about 10-12 hours and then cooling down. As a result, metal vapors precipitated on the fullerene powder to produce intercalated compounds of the following composition: Na_3C_{60} , Na_6C_{60} , K_3C_{60} , Li_6C_{60} and Li_3C_{60} .

Resulting alkali metals–fullerene compounds appeared to be more reactive with hydrogen under mild conditions without requiring additional catalyst. The experimental results of hydrogenation of alkali metal-doped fullerenes are shown in the Table 2.

Table 2. Hydrogen Storage Capacity of Na, K, Li - Doped Fullerenes at 200°C

Starting Material	Process parameters		Final Product	Wt.% Hydrogen
	Pressure, psi (MPa)	Time, hr		
1. Na ₃ C ₆₀	600 (~ 4)	6	Na ₃ C ₆₀ H ₁₉	2.30
2. Na ₃ C ₆₀	1500 (~ 10)	6	Na ₃ C ₆₀ H ₂₃	2.74
3. Na ₃ C ₆₀	2000 (~ 14)	6	Na ₃ C ₆₀ H ₂₆	3.19
4. Na ₃ C ₆₀	2000 (~ 14)	24	Na ₃ C ₆₀ H ₃₃	3.91
5. Na ₆ C ₆₀	1500 (~ 10)	24	Na ₆ C ₆₀ H ₃₆	3.99
6. K ₃ C ₆₀	600 (~ 4)	2	K ₃ C ₆₀ H ₅	0.58
7. K ₃ C ₆₀	1500 (~ 10)	2	K ₃ C ₆₀ H ₁₀	1.10
8. K ₃ C ₆₀	1500 (~ 10)	24	K ₃ C ₆₀ H ₂₉	< 3.0
9. Li ₃ C ₆₀	1500 (~ 10)	6	Li ₃ C ₆₀ H ₁₀	1.30
10. Li ₃ C ₆₀	1500 (~ 10)	24	Li ₃ C ₆₀ H ₂₄	< 3.0
11. Li ₆ C ₆₀	600 (~ 4)	2	Li ₆ C ₆₀ H _{7.5}	0.95
12. Li ₆ C ₆₀	1500 (~ 10)	6	Li ₆ C ₆₀ H ₁₇	2.17
13. Li ₂₀ C ₆₀	1500 (~ 10)	24	Li ₂₀ C ₆₀ H ₂₇	< 3.0

As it can be seen from this Table, the increase in pressure and time leads to higher weight percent hydrogen storage in fullerenes at 200°C. For example, hydrogenation of Na₃C₆₀ under 2000 psi for 24 hr results in 3.91% hydrogen storage without usage of any additional catalyst. The growth in hydrogen storage can also be observed if the concentration of alkali metal increases. Thus, switching to Na₆C₆₀ with higher content of sodium allows to reach 3.99% hydrogen storage at 1500 psi hydrogen pressure at the same duration of hydrogenation process. On the other hand, one can see that the hydrogen storage capability of K- and Li-doped fullerenes is considerably less than that of Na-doped fullerenes under similar conditions. As a result of this investigation, we can conclude that Na - doped fullerenes are more efficient in hydrogen storage than K and Li ones.

To verify the relationship between the level of hydrogenation and the alkali metal content, an attempt was made to produce highly intercalated fullerene compound with high concentration of alkali metal. According to Nalimova (1998) and Sklovsky (1998), the highest alkali metal content in fullerenes can be achieved using Li metal (Li₁₂₋₂₀C₆₀), although similar compounds with Na (for example, Na₁₆C₆₀) were also reported. Based on the high-pressure intercalation procedure described in these sources, a Li₂₀C₆₀ compound was produced by applying ~800,000 psi (5.5 GPa) pressure to the anvil cell containing stoichiometric amounts of fullerenes and Li, at 280°C. The produced compound was characterized by XRD, IR and ⁷Li NMR to confirm that no excessive Li was left after intercalation, and then tested for hydrogen storage. As a result of 24-hour exposure of this compound to hydrogen under 200°C at 1500 psi (~ 10 MPa), the level of hydrogenation did not exceed 3 wt.%, which is similar to the results obtained using Li₃C₆₀. This fact can be a result of Li clusters formation on the available C₆₀ sites, which means that not all the charge brought in

via Li atoms is transferred to fullerene cage, or can be attributed to the phase transition, which C_{60} undergoes at high pressures [Bashkin, 1994; Rao, 1997]. These findings suggest that an optimum concentration of the alkali metal might exist to allow maximum level of hydrogenation of Li_xC_{60} compounds. This possibility along with Na_xC_{60} compounds with $x > 6$, will be studied during the future work.

As it can be seen from the described results, modification of electronic structure of fullerenes by doping them with alkali metals does improve hydrogenation process at lower temperature and pressure. However, the dehydrogenation of the produced hydrides still remains a problem. According to the experimental data, only about 1.1 wt.% of hydrogen was released by heating a hydrogenated sample of $Na_3C_{60}H_{33}$ to $200^\circ C$ in vacuum for 6 hours. During the future research effort, the effect of a catalyst on dehydrogenation of such compounds will be studied.

In addition, an attempt was made to intercalate fullerenes with Cesium in order to facilitate charge transfer. It is realized, however, that in order to compensate for the weight increase due to the higher molecular weight of Cs, such systems will have to be able to achieve higher hydrogen storage capacity. Cs_3C_{60} was prepared by reaction of C_{60} with Cs in liquid ammonia, followed by heating at $150^\circ C$ [Palstra, 1995]. This route circumvents formation of the energetically more stable Cs_1C_{60} and Cs_4C_{60} phases. According to the procedure described in this source, Cs metal and C_{60} powder in a stoichiometric ratio of 3:1 were cooled in an evacuated container by a dry-ice/isopropanol slush. Anhydrous NH_3 was condensed onto Cs/ C_{60} mixture through a vacuum line. The C_{60} powder completely dissolved in the liquid NH_3 , indicating charge transfer from Cs to C_{60} (pristine C_{60} is insoluble in liquid NH_3). After about half an hour, NH_3 was evaporated from the solution by heating up the container to $150^\circ C$ under vacuum, conditions sufficient to remove NH_3 from $NH_3Cs_3C_{60}$. Heating was stopped when no more NH_3 evolved from the container. The produced compound was exposed to hydrogen gas at 1500 psi (~ 10 MPa) at $200^\circ C$ for 6 hours resulting in ~ 3.3 wt% hydrogen storage based on preliminary data. These data will also be verified during future activities on the project.

Physical Adsorption of Hydrogen on Fullerenes

Enhancement of physical adsorption on fullerenes can be achieved by structural fragmentation resulting in opening of fullerene cage. According to the activation procedure developed at MER, fullerenes undergo oxygen treatment followed by CO_2 activation, which results in a dramatic increase in surface area (from ~ 4 m^2/g to almost $3,000$ m^2/g) while maintaining a narrow pore size distribution between 2 to 20 \AA . The bulk density of so treated fullerenes varies between 0.9 and 1.2 g/cc. These characteristics perfectly agree with requirements for ideal hydrogen adsorbent derived by Chahine (1996).

The hydrogen storage capacity of activated fullerenes was measured using an original computer-controlled experimental setup, which allows precise measurement of adsorption isotherms in wide range of temperatures and pressures. The comparative hydrogen adsorption isotherms obtained using activated and untreated fullerenes are shown in Fig. 4.

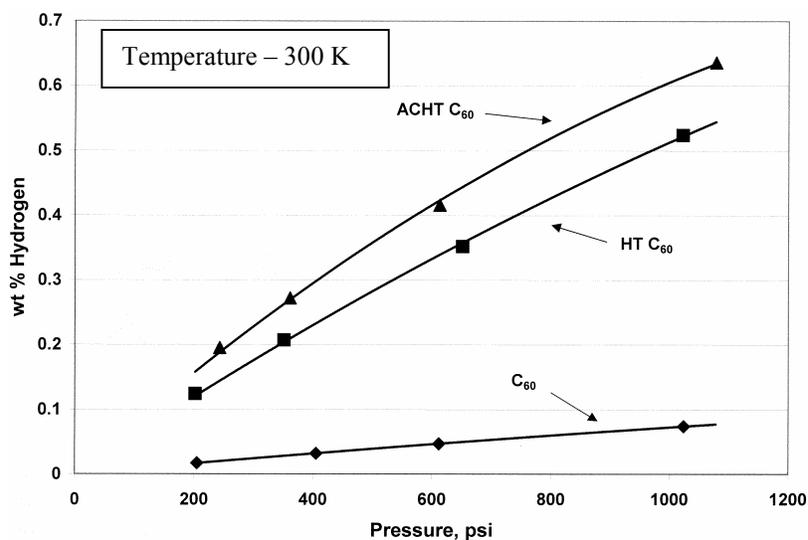


Figure 4. Physical Adsorption of Hydrogen on Fullerenes

As it can be seen from the graph, about 0.64 wt.% hydrogen storage was achieved on oxygen and CO₂ activated fullerenes (ACHT C₆₀) at ~1000 psi and ambient temperature as opposed to 0.51 wt.% on just oxygen-treated fullerenes (HT C₆₀) and 0.08 wt.% on untreated fullerenes (C₆₀) respectively. Considering the density of ACHT C₆₀ of 0.9 g/cc and HT C₆₀ of 1.2 g/cc, the volumetric hydrogen storage capacity of these materials translates into 5.8 g/l and 6.2 g/l respectively.

The obvious advantage of fullerenes is their ability to be pelletized without any binder. In this case, the packing density may reach 1.5 g/cc or higher, increasing the volumetric capacity to about 9.5 g/l. In combination with moderate heat of adsorption (~10 kJ/mol), this makes fullerenes very attractive candidates for physical hydrogen adsorbents.

In some way, the mechanism of hydrogen adsorption using structurally modified fullerenes is similar to that on single-wall nanotubes (SWNT). Structural optimization of SWNT calls for open-ended short-length nanotubes, which are supposed to facilitate hydrogen access to the internal cavities. However, similar structure is achieved by utilizing fragmentation of fullerenes. This may suggest that the hydrogen storage capacity of both materials at the same conditions should also be similar, which is below 1 wt% so far.

Conclusions and Future Work

Based on the performed work, MER has developed a great deal of new knowledge about the physics and chemistry of fullerenes, and their potential use as advanced hydrogen storage materials. It is clear that the major problem preventing the required level of reversible hydrogenation at moderate conditions is associated with dehydrogenation of fullerene hydrides characterized by high level of activation energy as well as high thermal stability caused by low enthalpy of formation. The latter can be dealt with by increasing the levels of initial hydrogenation of fullerenes. To lower the activation energy barrier, the optimization of the catalytic system as well as electronic structure of fullerenes is required. Based on the results achieved earlier, the following activities are planned for the future research.

1. MER will continue optimizing charge transfer using alkali metal-doped fullerenes by altering dopants and varying their content. In addition, the catalytic approach will be applied to facilitate hydrogen exchange in such compounds. One of the options will be using Na_xC_{60} in conjunction with TiCl_3 , which is similar to the approach undertaken in recent studies of NaAlH_4 and Na_3AlH_6 .
2. MER will further investigate and evaluate Cs-doped fullerenes to establish Cs effect on hydrogen exchange at moderate temperatures in this system.
3. MER will continue to study physical adsorption on activated fullerenes to establish the practicality of using this method in commercial systems.
4. MER will perform cost analysis to estimate the projected cost of the fullerene-based hydrogen storage option.

In terms of commercialization, MER has moved far forward in attempting price reduction of fullerenes by establishing *Fullerene International Corporation* (www.fullereneinternational.com), a joint venture with Mitsubishi Corporation and RCT. As a result of this joint effort in optimizing process parameters and scaling up the production, the price of fullerenes and fullerene-related materials is expected to drop significantly (\$30 – 60 per 1 kg over the next 3 years), which will make them practically available worldwide.

Acknowledgments

Current research project is being sponsored by US DOE Hydrogen Program, Contract DE-FC36-00G010532.

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