

IV.C.2 Electron-Charged Graphite-Based Hydrogen Storage Material

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Subcontractors:

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4201 W. 36th Street
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Projected End Date: June 30, 2009

(E) Charging/Discharging Rates

(Q) Reproducibility of Performance

Technical Targets

This project is conducting research on the graphite-based materials for hydrogen storage with external electronic charges to increase hydrogen storage capacities and charge/discharge rates that meet the following DOE 2010 hydrogen storage targets:

- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L
- Durability/operability: 1,000 cycles
- Cost: \$4/kWh net

TABLE 1. Progress Toward Meeting DOE On-Board Hydrogen Storage Targets

Storage Parameter	Units	2010 System Target	FY 2006 material status*
Specific Energy	kWh/kg	2.0	0.33
Energy Density	kWh/L	1.5	0.41
Adsorption/desorption Temperature	°C	-30/50	-20/120

*GTI material packing density: 1.26 g/cm³

Objectives

- Expansion of the graphite layers and generation of small particles to allow access for hydrogen adsorption.
- Metal intercalation in the graphite layers to increase back-donated electron charges onto/into the carbon, so the hydrogen adsorption becomes combined physisorption and chemisorption.
- Addition of electron charge during hydrogen filling to increase hydrogen storage with discharge to release hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability

Accomplishments

- Demonstrated the hydrogen storage capacity 0.8~1.0 wt% or 12.6 g/L of graphite-based materials at 20°C adsorption and 100°C desorption from 6 bar to 10 bar pressure.
- Achieved 4.5Å space between graphite layers. The surface area increased from 9 m²/g to 700 m²/g. The expanded graphite enables metal intercalation into the graphite layers to stabilize the expansion and prevent the spring-back of the layers. The metal intercalation provides more electrons to graphite for hydrogen adsorption and the graphite expansion provides space for hydrogen storage.
- Demonstrated the ability of external electron charges to alter hydrogen storage behavior. The pressure-concentration-temperature (PCT) curves of the graphite-based materials show that the positive charges at 5 V versus ground reduce the hydrogen storage 1.65x10⁻⁴ mole/g and negative charges at -5 V versus ground increase the hydrogen storage 1.65x10⁻⁴ mole/g at 700 psig pressure and room temperature.

Introduction

Hydrogen is a non-polar molecule and it is physisorbed on carbon-based materials. The carbon material is also a non-polar substrate. The non-polar hydrogen molecules adsorbed on a non-polar carbon substrate are not dissociated and the force between these two non-polar species is basically the weak Van der Waals force. However, as previous research has shown, the adsorption force could increase if the substrate could be polarized. The polarization of the substrate can be done in two ways. One way is to deposit, or intercalate electron-rich materials, such as metals, or “electron-hungry” materials, such as nitrogen, phosphor and other atoms (Figure 1). This is possible with the graphite layer expanding techniques developed by Superior Graphite.

Another way is to polarize the entire substrate by adding an electrical potential similar to capacitors. In this concept, either intercalation or charging alone is not sufficient to achieve high storage amounts. Therefore, combining a method of polarization with the modified expanded intercalated graphite structure could have an excellent chance to meet the DOE hydrogen storage targets at ambient temperature. Although the electrochemical method can also add charges to the hydrogen storage material [1], an electrolyte is also needed in the electrochemical absorption, which we think is not feasible for hydrogen storage for transportation.

Approach

1. Select graphite and study graphite expansion and intercalation conditions. The goal is to prepare specially processed graphite materials and to modify their structure. GTI and Superior selected from many available natural flake graphite materials and metal candidates. Superior processed and prepared various samples of the modified graphite with intercalated

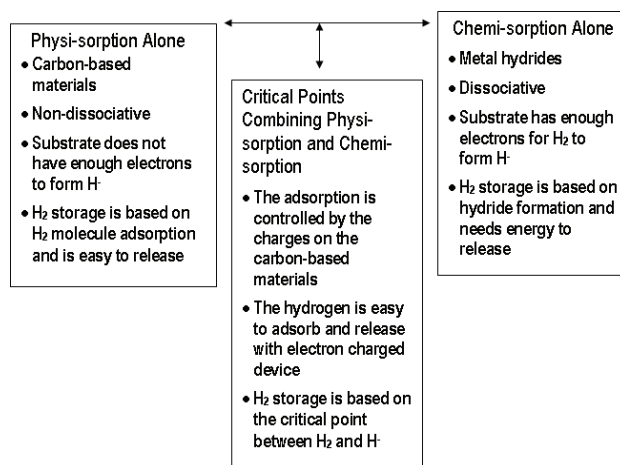


FIGURE 1. Critical Points Combining Physisorption and Chemisorption

metals. Several specially modified graphite types, particle sizes, and compositions were prepared for tests. Different shapes of the graphite particles may affect the hydrogen storage. GTI and Superior explored both natural and synthetic graphites with different shapes and characteristics for modification and storage ability.

2. Construct an electron charge device and evaluate the GTI electron charge concept with the modified graphite materials over a range of parameters. We constructed an electron charge device, with applied voltage measurements, and the appropriate necessary insulated sample holders. Measurement of the hydrogen storage amount versus the charge (charge device voltage) was conducted. Moisture, temperature, and gas composition will be measured during multiple trials with several samples. The temperature changes upon fill and discharge will be measured to assess thermal management needs for a practical device.

Results

A. Storage Material Preparation

GTI worked with its partners, Superior Graphite and specific equipment at the University of Massachusetts to develop the graphite-based hydrogen storage materials. Figure 2 shows the procedures to produce the expanded graphite based materials and to increase the hydrogen storage capability. Superior Graphite and the University of Massachusetts carried out the material preparation and measured the surface area, which increases from 9 m²/g to 700 m²/g using the Bruner-Emmett-Teller method. We have already achieved 4.5 Å space between graphite layers.

The expanded graphite materials are intercalated with metals to increase electron charges on the graphite

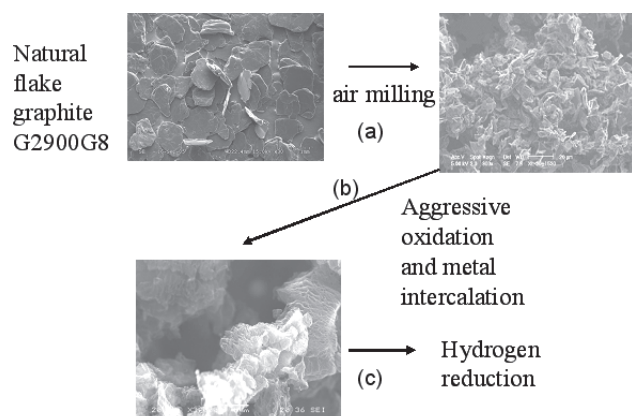


FIGURE 2. Development Scheme of Graphite-based Hydrogen Storage Materials (a) air-milling to decrease particle size, (b) oxidative expansion and intercalation to increase the space between graphite layers, and (c) hydrogen reduction to remove oxides

substrates. A mechanic-diffusion method is used to insert Li, Mg, and other metal candidates onto/into graphite layers. 0.1% Pd was added into the graphite as a catalyst and one of the spillover metals.

B. Hydrogen Storage Material Lifetime Cycles

Reversibility of hydrogen charge and discharge is essential for on-board hydrogen storage. Before we test the electron-charge effect on the graphite-based materials, we tested the reversibility of the hydrogen charge and discharge. A dynamic thermo-gravimetric analyzer (TGA) was used to determine the reversibility of the hydrogen storage materials. This dynamic analysis eliminates the water condensation effect on the test. The test chamber is always purged by hydrogen. Figure 3 shows the hydrogen adsorption/desorption cycles of one of the graphite-based materials. The scan temperature was from 25°C to 100°C with a scan rate of 5°C/min at ambient pressure. The deviation of the weight measurement is $\pm 1 \mu\text{g}$. The graphite-based material showed good reversibility although the hydrogen storage

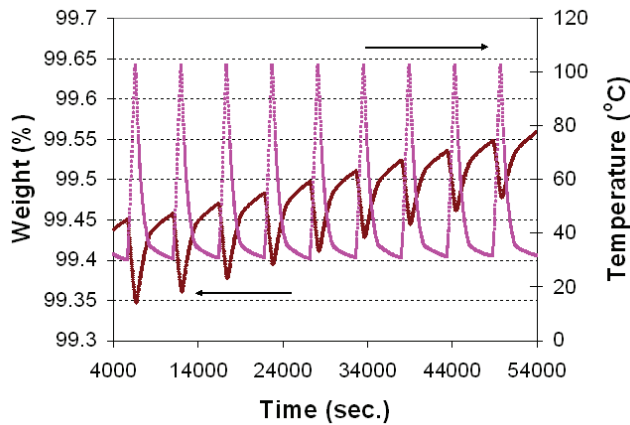


FIGURE 3. Hydrogen Adsorption/Desorption Cycle Tests of the Graphite-based Materials

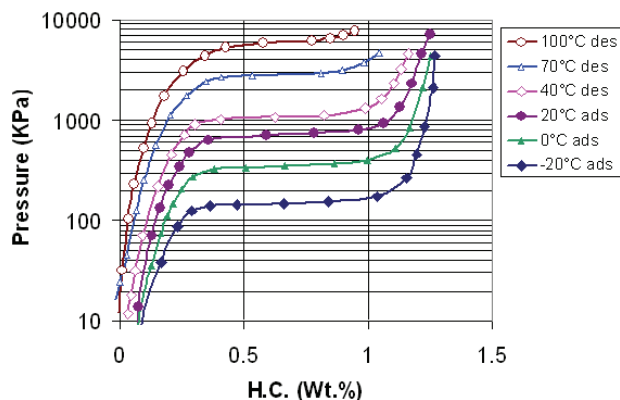


FIGURE 4. PCT Curves of the Graphite-Based Materials

residue increases. This material was also tested in a Sievert device to obtain PCT curves. Figure 4 shows the hydrogen storage capacity is approximately 0.8 to 1.0% or 12.6 g/L at 20°C between the pressures of 6 bar to 10 bar.

C. Electron-Charge Effect on Hydrogen Storage

After obtaining 0.8 to 1 wt% hydrogen storage, GTI assembled an electron-charge device to verify the electron-charge concept. The diagram of the electron-charged hydrogen storage device is described in Figure 5. An organic polymer with a glass temperature of 180°C was coated on the inner-wall of the chamber. The hydrogen storage material was added into the chamber and 5 V was applied between the chamber body and the Ni wire. Figure 6 shows the PCT curves under different polarization potentials. The applied electron-charge mainly affects the pressure-dependent adsorption regions. And, repeatably, negative charges act to shift the PCT to the right (increase hydrogen adsorption) and positive charges act to shift the PCT curve to the left (decrease hydrogen storage). GTI plans to test the electron-charge effect on the different hydrogen storage materials.

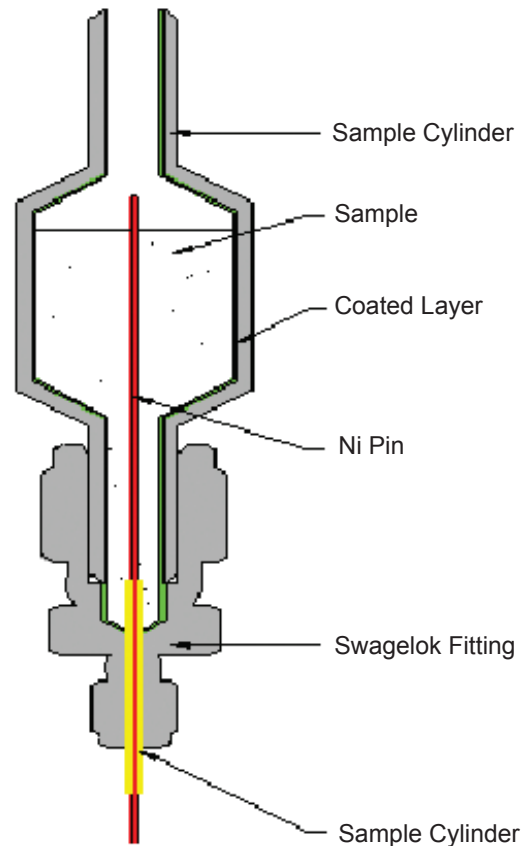


FIGURE 5. A Device for Electron-charged Hydrogen Storage Material Test

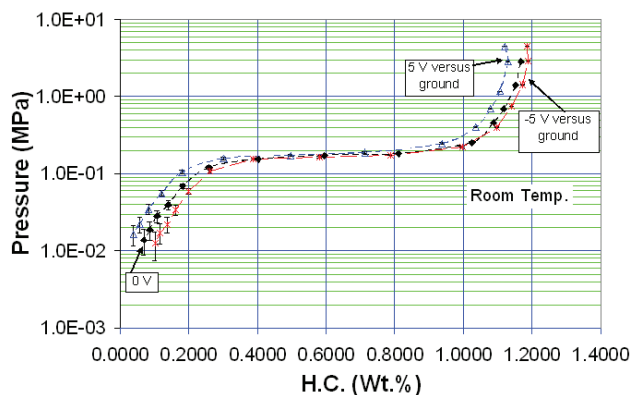


FIGURE 6. Electron-Charge Effect on Hydrogen Storage

The PCT shift is related to the electronic structure of the substrate. Electron-rich material needs positive charges and electron-poor material requires negative charges. Through the use of an external electron-charge device, the adsorption/desorption rates can be improved by adjusting the external electronic charges.

Conclusions and Future Directions

- Demonstrated hydrogen storage capacity 0.8~1.0 wt% of graphite-based materials.
- Achieved 4.5 Å space between graphite layers.
- Demonstrated that the external electron charges affect hydrogen storage. The PCT curves of the graphite-based materials show that the positive charges reduce hydrogen storage and negative charges increase hydrogen storage. The PCT shift is related to the electronic structure of the

substrate. Electron-rich material needs positive charges and electron-poor material needs negative charges. External charge shifts the chemisorption to physisorption and shifts physisorption to chemisorption with different charges.

- Examine different hydrogen storage materials, such as carbon-based materials, metal hydrides, and chemical hydrides, in the electron-charge device. In order to distribute the electronic charge evenly in the chamber, a hydrogen storage polymer will be mixed with the hydrogen storage material to reduce the radial effect of charges. This polymer would be a bridge between storage powders.
- Improve graphite-based hydrogen storage materials to increase hydrogen storage capacities and reversibility. The encouraging results (4 wt% hydrogen storage) from the DOE carbon center leads us to pursue the material storage rate of 4 wt% and the external charge addition of 2 wt% in the 2007 period.
- Continue to screen different candidates for hydrogen storage.

FY 2006 Publications/Presentations

1. A poster presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 2006).
2. A patent application was filed and published.

References

1. Schlapbach et al in *Electrochemical and Solid State Lett.*, 2, 30 (1999).