

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

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Technical Targets

This project involves conducting research on 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

Progress Toward Meeting DOE On-Board Hydrogen Storage Targets

Storage Parameter	Units	2010 System Target	FY 08 material status*
Specific Energy	kWh/kg	2.0	0.44
Energy Density	kWh/L	1.5	0.49
Adsorption/Desorption Temperature	°C	-30/50	-20/120

*GTI material packing density: 1.12 g/cm³

Objectives

- Preparation of high surface area carbon-based materials and generation of small particles to allow access for hydrogen adsorption.
- Electron-rich material doping into high surface area carbon to increase 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
- (E) Charging/Discharging Rates
- (Q) Reproducibility of Performance

Accomplishments

- Applied charge control agent (CCA) and charge transfer agent to the hydrogen storage material to improve hydrogen storage capacity.
- Combined the external charge and internal charge to control hydrogen storage kinetics.
- Demonstrated access hydrogen storage capacity of 1.325 wt% carbon-based materials at 25°C adsorption and 100°C desorption at ambient pressure.
- Demonstrated the ability of external electron charges to alter hydrogen storage behavior.



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 a 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. Electron-conductive polymers are also a choice.

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 of meeting the DOE hydrogen storage targets at ambient temperature.

Approach

Select carbon-based materials and prepare high surface area carbon with electron-rich materials.

The goal is to prepare specially processed carbon-based materials and to modify their structure. GTI has prepared several high surface area carbon-based materials for electron-charge evaluations. The carbon materials are (1) coconut charcoal; (2) air-gel carbon; (3) liquid-gel carbon; (4) AMTI high surface carbon, 1.12 g/cc and pore size 0.5 to 0.8 nm with surface area more than 1,500 m²/cc; and (5) SUNY high surface area carbon. GTI synthesized coconut charcoal, air-gel carbon, and liquid-gel carbon.

The carbon materials were coated with the CCA as shown in Figure 1. The net charge of the material is zero; however, the charge will be distributed on the surface of the powders under an electrostatic field. Table 1 lists the charge control agent properties. The CCA has a charge retention rate of $-\mu\text{C}/\text{g}/\text{min}$, which enables enough time for hydrogen adsorption under an electrostatic field.

TABLE 1. Characterization of the Charge Control Agent*

Item	Results
Appearance	Black powder
Charge measurement for 60 seconds ($-\mu\text{C}/\text{g}$)	40.0
Average particle size (μm)	1.58
Apparent specific gravity (g/cm^3)	0.295

*Obtained from a Japanese company

Construct and modify an electron charge device and examine the electron charge effect on the hydrogen storage capacities of the carbon based materials. 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.

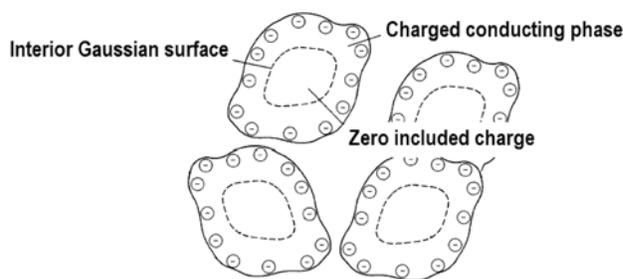


FIGURE 1. Charge Control Agent Modified Carbon Materials for Hydrogen Storage

Results

A. Hydrogen Storage Tests

Hydrogen adsorption on carbon requires a very high surface area. However, only a high surface area might not be enough to store hydrogen at ambient temperature. GTI worked with its partners to develop high surface carbon with electron-rich material doping. The doping material is a polymer-based CCA. Figure 2 shows the material analysis using scanning electron microscopy (SEM). As shown, carbon is the main component and silicon is the supplemental component in the material.

The materials were tested in a dynamic thermal gravimetric analyzer (TGA). The dynamic TGA precisely measures the hydrogen storage capacities without water condensation affecting the measurements. Figure 3 shows the TGA data of the hydrogen storage samples under different doping levels of the electron-rich materials. The scan temperature was from 25°C to 220°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 temperature of the hydrogen desorption was approximately 60°C. As shown in Figure 3, more electron-rich material doping increases the hydrogen storage capacity; however, the carbon-based precursor may not accept more doping if the mole ratio is more than 1:4. More tune-ups are needed.

B. Electron-Charge Effect on Hydrogen Storage

GTI assembled and modified an electron-charge device to test the electron-charge effect. The hydrogen storage material was added into the chamber and 5 V was applied between the chamber body and the Ni wire. Figure 4 shows the pressure-concentration-temperature (PCT) curves under different polarization potentials. The applied electron-charge mainly affects the pressure-dependent adsorption regions. Repeated, negative charges acted to shift the PCT to the right (increase hydrogen adsorption) and positive charges acted to shift the PCT curve to the left (decrease hydrogen storage). However, we could not perform a 77 K experiment

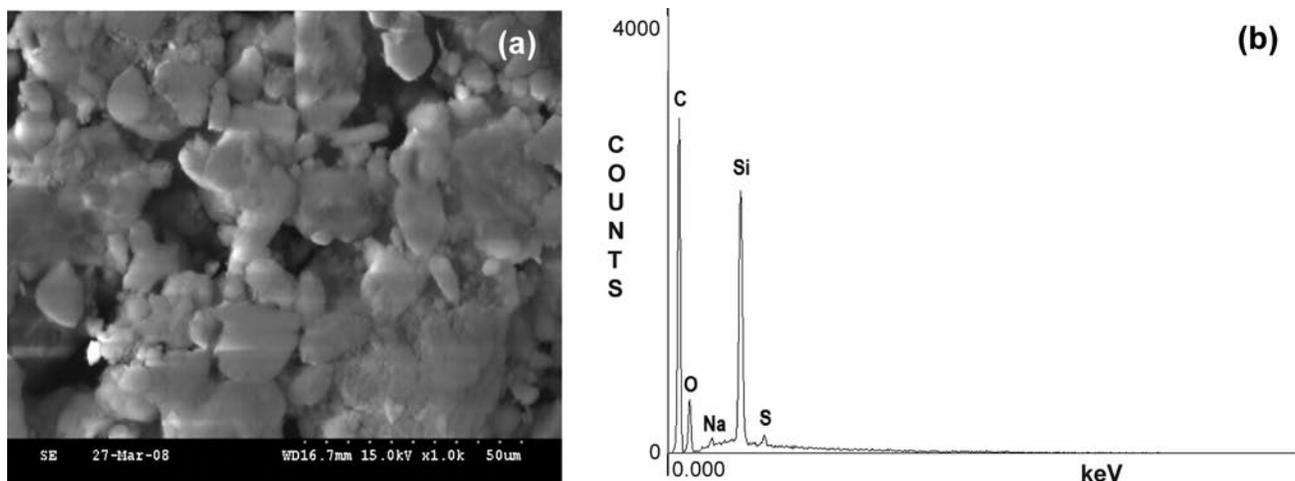


FIGURE 2. SEM Analysis of the Carbon-based Material (a) SEM Image of the Carbon-based Material with CCA and (b) Element Mapping of the Material

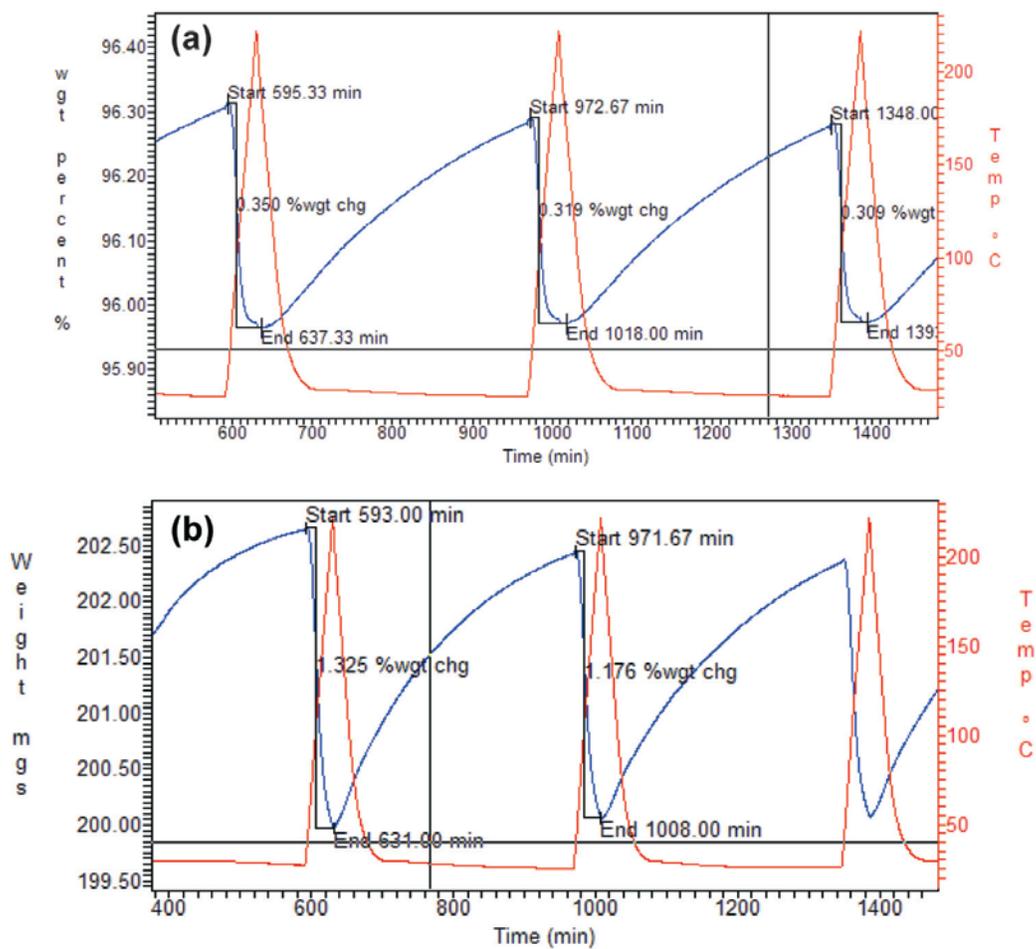


FIGURE 3. Thermal Gravimetric Analysis of the Hydrogen Storage Materials under Different Doping Levels of the Electron-rich Element (a) 1:1 and (b) 1:4 (Moles of precursor : moles of doping material)

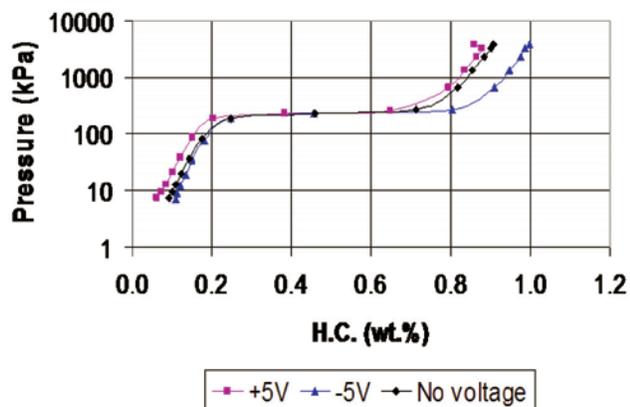


FIGURE 4. External Charge Effect on the Hydrogen Storage Capacities

because the insulation on the electrode could not tolerate the low temperature. An electrical short was found in the system.

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 the hydrogen storage capacity 1.325 wt% of graphite-based materials.
- Electron-rich material doping increases the hydrogen storage capacity.
- Demonstrated that the external electron charges affect the hydrogen storage. The PCT curves of the graphite-based materials show that the positive

charges reduce the hydrogen storage and negative charges increase the 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 (1) coconut charcoal; (2) air-gel carbon; (3) liquid-gel carbon; (4) AMTI high surface carbon, 1.12 g/cc and pore size 0.5 to 0.8 nm with surface area more than 1,500 m²/cc; and (5) SUNY high surface area carbon. A CCA was used to distribute charges uniformly.
- Additional information regarding the electron-charge device and the material properties of the carbon-based material (pore size, density, surface area, etc.) that are best suited for this technique should be investigated and results reported.
- Continue to screen different candidates for hydrogen storage.

FY 2008 Publications/Presentations

1. A poster presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (June 2008).
2. A patent application was published.

References

1. Schlapbach et al in *Electrochemical and Solid State Lett.*, 2, 30 (1999).
2. Simonyan et al in *Journal of Chemical Physics*, 111(21), 9778 (1999).