IV.F.5 Electron Charged Graphite-Based Hydrogen Storage Material

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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 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

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:

- System Gravimetric Capacity: 0.045 kg H_2/kg system
- System Volumetric Capacity: 0.028 kg H_2/L system
- Durability/Operability: 1,000 cycles
- Cost: $4/kWh net

Table 1 shows progress toward meeting the DOE on-board hydrogen storage targets.

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

Storage Parameter	Units	2010 System Target	FY09 system*
System Gravimetric Capacity	kg H_2/kg system	0.045	0.028
System Volumetric Capacity	kg H_2/L system	0.028	0.101
Storage System Cost	$/kg H_2	133	>1200
Adsorption/desorption Temperature	°C	-30/50	-20/120

*GTI metal hydride-based material (3 wt% hydrogen storage) with tank at 1,000 psi

Accomplishments

- Worked with partners to explore high surface carbon (AX-21 and other high surface area carbons) for hydrogen storage with the help of electrostatic charges.
- Repeated the electron charge effect experiments on the hydrogen storage capacity of materials and conclude that positive charge increases hydrogen storage on metal-based material and negative charge increases hydrogen storage on non-metal hydrogen storage materials.
- Tested the external charge effect on the hydrogen charge/discharge kinetics, especially on-site regeneration of borane-nitride materials.
- Designed a practical 11-liter hydrogen storage charge system with electron-charge and cooling/heating for hydrogen uptake and release. The system hydrogen storage capacity is 0.028 kg H_2/kg system and 0.101 kg/liter system.

Introduction

Hydrogen adsorption on metal-based materials suffers slow kinetics for hydrogen uptake and release with storage gravimetric capacity 3.3 wt% at material base. Hydrogen molecules are physisorbed on carbon-based materials at temperatures as low as 77 K. The metal-based materials are polar substrates while the carbon materials are non-polar substrates. 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. The non-polar hydrogen molecules adsorbed on a polar (metal) substrate generate an electron spillover effect. Whatever the substrate is, polar or non-polar, the external electrical force could polarize the substrate surface to change the hydrogen adsorption capacity and kinetics.

Approach

- Test and evaluate cycles for hydrogen storage:
  - Modify the electron charge distribution structure (framework structure) to obtain a 50% hydrogen storage rate increase.
  - Fueling kinetics study: does the electron charge make desorption fast?
  - Theoretical calculation: how much charge is needed to get 6 wt%?
- Optimize charge control agent (CCA) and charge transfer agent (CTA) to help polarize storage materials.
- Characterize the electron device and the material properties of the carbon-based material with CCA/CTA (pore size, density, surface area, etc).
- Scale-up to an 11-liter tank for fueling demonstration to show 50% hydrogen storage increase.

Results

A. Hydrogen Storage Tests with/without Electrostatic Charge

1. System Design

The external electron-charge has been demonstrated to have an effect on the hydrogen storage kinetics and capacities. Figure 1 displays the design of an electron-charged hydrogen storage system (11-liter tank). In this system, a stainless steel coil with polymer coating insulation is inserted into the tank. The functions of the stainless steel coil are conducting electron-charge and cooling/heating the hydrogen storage materials.

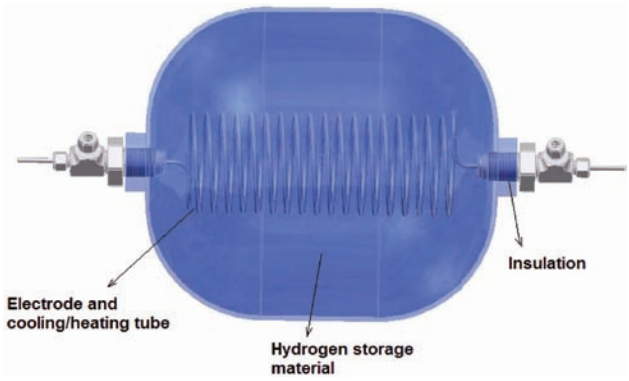

FIGURE 1. Electron-Charged Hydrogen Storage System Design

A similar 10 ml system is used for material screening and hydrogen storage tests.

2. Hydrogen Storage Tests

The electron-charge hydrogen storage system has been scanned to check for any internal short under hydrogen storage pressure and found that even if the voltage goes to 1,000 volts, the leak current is very small as tested in the milli-ampere scale. Therefore all the tests using this system show the electro-static non-Faradaic effect on the hydrogen storage.

A metal-modified AX-21 carbon mixed with CCA was used to test the electron-charge effect on hydrogen storage. Figure 2 exhibits the external electron-charge effect on the hydrogen storage pressure concentration isotherm curves. At room temperature, positive charge increased adsorption on the metal modified AX-21.

Borane-nitride is a very attractive material for hydrogen storage. Its hydrogen storage capacity is theoretically more than 10 wt%. However, the hydrogenation and dehydrogenation kinetics are too slow. At 80°C, the hydrogen release takes more than 24 hours to release 5.70 wt%.

At 900 psi, the decomposition of borane-nitride for 1.5 wt% takes 2.5 hours without electrical charge and only 40 minutes with negative charge as shown in Figure 3. The decomposition rate under electrical charge at different pressures will be generated. Figure 4 shows the electrostatic effect on hydrogen storage with 1.00 g borane-nitride and 0.05 g catalyst at 80°C. The threshold point occurs when pressure increases to 6 MPa with negative charge. These results once again verified that negative charge increases the hydrogen storage again.

B. High Surface Carbon for Hydrogen Storage

The cooperation with State University of New York (SUNY) at Syracuse helps us to develop the hydrogen storage electron-charge system. GTI tested eight samples

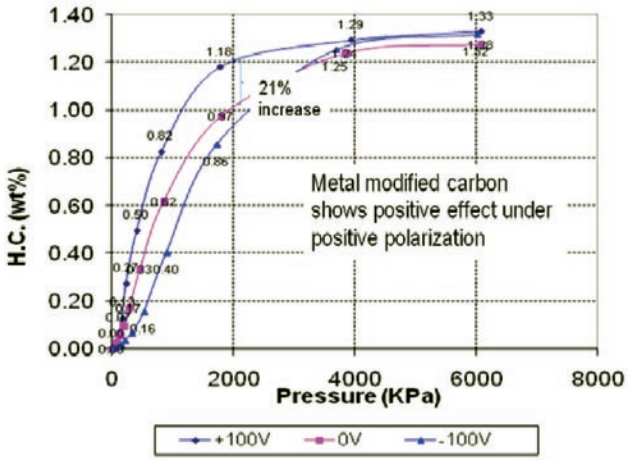

FIGURE 2. Electro-Static Voltage Effect on Hydrogen Storage at Room Temperature

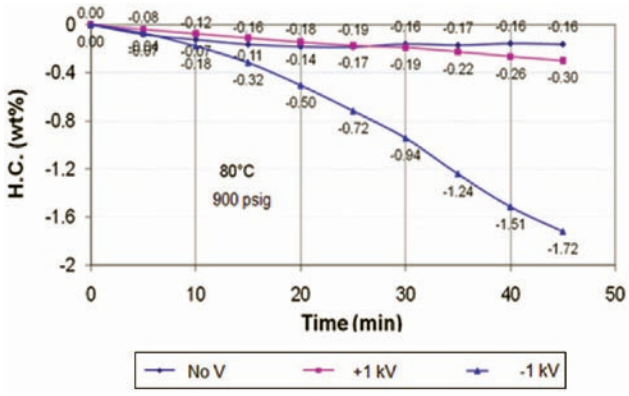

FIGURE 3. Electro-Static Voltage Effect on Hydrogen Release of Borane-Nitride at 80°C and 900 psi H_2 Pressure

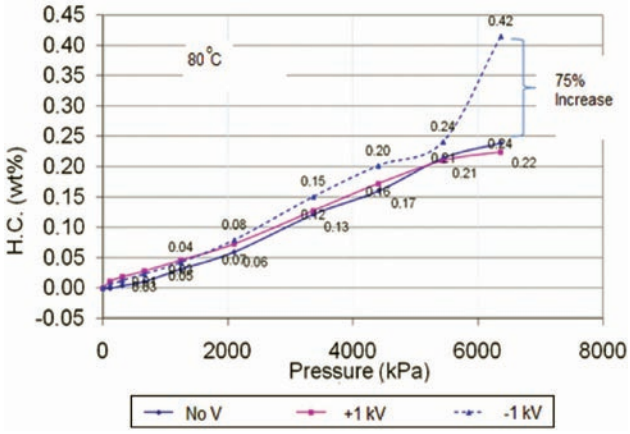

FIGURE 4. Electro-Static Voltage Effect on Hydrogen Storage Material B-N at Room Temperature

and the results are summarized in Table 2. The best hydrogen storage gravimetric capacity is 7.0 wt% at 77 K.

TABLE 2. Summary of SUNY samples at 6,300 kPa

Sample name	0°C (wt%)	77 K (wt%)
APPANNI(2)	0.52	6.5
APKI6S2	0.40	7.0
MK775	0.44	5.8
PK-NaH-1-1	0.38	4.4
APTPN1	0.49	6.4
N24Ma1045	0.33	4.8
N24	0.52	7.0
APK25N1	0.77	6.0

Conclusions and Future Directions

- The electron charge effect experiments on the hydrogen storage capacity of materials conclude that positive charge increases hydrogen storage on metal-based material and negative charge increases hydrogen storage on non-metal hydrogen storage materials.
- The external charge shows the effects on the hydrogen charge/discharge kinetics, especially on-site regeneration of borane-nitride materials – 75% increase at 600 psig.
- A practical 11-liter hydrogen storage charge system with electron-charge and cooling/heating for hydrogen uptake and release was designed. The system hydrogen storage capacity is 0.028 kg H_2/kg system and 0.101 kg/liter system.
- Test 11-liter hydrogen storage system for practical applications.

FY 2009 Publications/Presentations

1. A poster presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 20, 2009).

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).