

IV.C.3 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 Fuel Cell 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 H₂/kg system
- System Volumetric Capacity: 0.028 kg H₂/L system
- 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	Fiscal Year 2009 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	>1,200
Adsorption/Desorption Temperature	°C	-30/50	-20/120

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

Accomplishments

- Tested a water cooling/heating system for hydrogen storage and release.
- Repeated the electron charge effect experiments on the hydrogen storage capacity of materials under water cooling and heating.
- Tested the in situ regeneration of borane-nitride materials.



Introduction

Hydrogen adsorption/desorption of metal-based materials with storage gravimetric capacity of 3.3 wt% of base material have slow kinetics with chemisorption. For comparison, 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 weak van der Waals force. The non-polar hydrogen molecules adsorbed on a polar (metal) substrate generate an electron spillover effect on hydrogen adsorption. Whether the substrate is polar or non-polar, the external electrical force could polarize the substrate surface to change the hydrogen adsorption capacity and kinetics. In the last annual report, it was concluded that positive charge increases hydrogen storage on metal based material and negative charge increases hydrogen storage on non-metal hydrogen storage materials. This year, we focus on the substrate and regeneration of hydrogen storage materials.

Approach

- Test and evaluate the hydrogen storage system with cooling/heating:
 - 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%?
- Build a system with water cooling and heating to enhance hydrogen storage and release rate.
- 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

External electron-charge has been demonstrated to affect hydrogen storage kinetics and capacities. Figure 1 shows the design of our electron-charged hydrogen storage system with cooling/heating feature. In this system, a stainless steel coil with polymer coating as insulation is inserted into the tank. The stainless steel coil conducts electron-charge and cools/heats the hydrogen storage materials. A similar system with 10 ml capacity is used for material screening and hydrogen storage tests.

2. Hydrogen Storage Tests

The electron-charge hydrogen storage system was checked for any internal short under hydrogen storage pressure. It was determined that even if the voltage goes to 1,000 volts, the leak current is very small and would

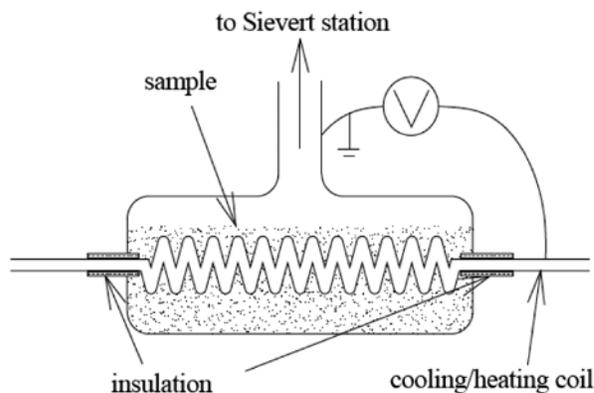


FIGURE 1. Electron-Charged Hydrogen Storage System with Cooling and Heating

not affect experimental results. Therefore all the tests using this system show the electro-static non-Faradaic effect on the hydrogen storage due to low Faradaic current.

Figure 2 is a pressure-composition-isotherm (PCI) curve of a metal-based hydrogen storage material during cooling and heating modes. Hydrogen is adsorbed during cooling and released during heating as expected. The system was verified for use in external charge experimental tests.

The hydrogen storage system with cooling/heating was connected to an external electrical charge device to determine the effect of external charges on hydrogen storage. Figure 3 shows the PCI curves of the metal-based hydrogen storage material under positive charge (a) and negative charge (b) during cooling and heating. PCI curves with electrical charges shift and shows increased hydrogen storage. However the shift seems to be independent to the charge polarities. It could be due to activation of storage material by external charges. The key is to look for a hydrogen storage material that

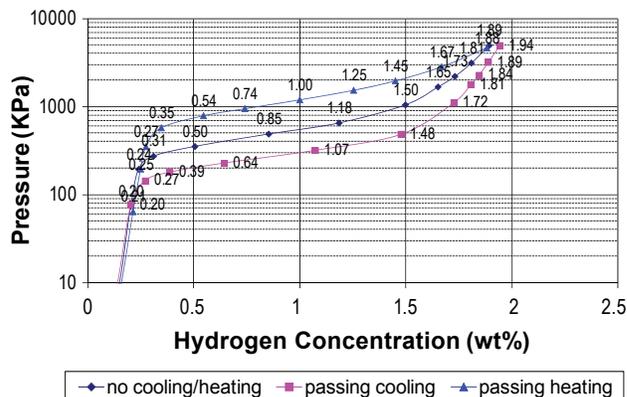
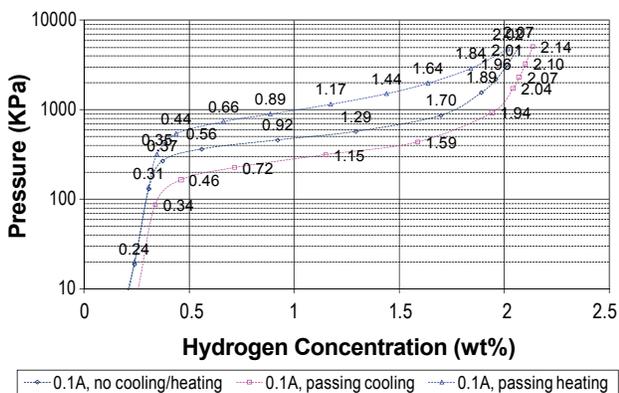
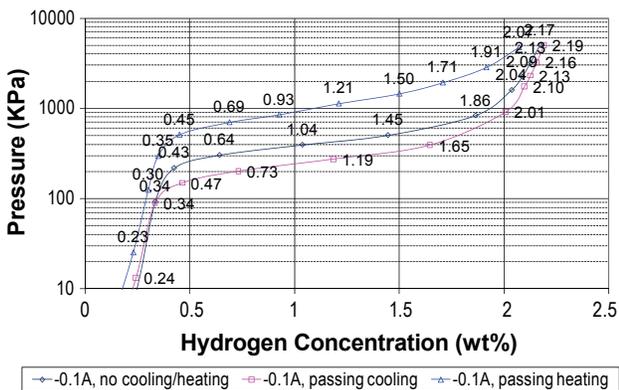


FIGURE 2. Cooling/Heating Effects on Hydrogen Storage



(a)



(b)

FIGURE 3. Cooling/Heating Effects on Hydrogen Storage at 0.1 A External Charge

has high storage capacity and is sensitive to external charge to promote hydrogen uptake. Borane-ammonia is one of the materials we investigated.

Its hydrogen storage capacity is theoretically more than 10 wt%. However, its hydrogenation and dehydrogenation kinetics are slow. Catalytic regeneration of borane-ammonia was pursued to improve the kinetics. Table 2 lists the hydrogen storage capacity under different catalyst as determined by thermal gravimetric analysis (TGA).

3. Regeneration of Borane-Ammonia

The electrochemical activity of BH₃NH₃ was tested in diglyme because of its high boiling point of 162°C and capability to chelate small cations. For all supporting electrolyte used, when heated near 100°C, the BH₃NH₃ expanded greatly. This also had an effect on cyclic voltammograms (CVs). Figure 4 shows the CV for BH₃NH₃ in diglyme.

TABLE 2. Borane-Ammonia Regeneration under Different Catalysts by TGA

Sample content	Weight loss after 150°C (%)
BH ₃ NH ₃ :Ni (1:1)	13.828
BH ₃ NH ₃ :SAPO (1:1)	15.292
BH ₃ NH ₃ :BiPbSnCd (1:1)	10.26
BH ₃ NH ₃ :BZSM5 (1:1)	10.663
BH ₃ NH ₃ :BZSM5 with Rh (1:1)	9.742
BH ₃ NH ₃ :KA (1:1)	13.555
BH ₃ NH ₃ :BiSn (1:1)	9.008
BH ₃ NH ₃ :LaNi ₅ (1:1)	8.583
BH ₃ NH ₃ :FeTiO ₃ :SAPO (2:1:1)	10.92
BH ₃ NH ₃ :Fe _x N:SAPO (2:1:1) _{x=2-4}	12.362
BH ₃ NH ₃ :SiC:Rh (15:11:4)	8.662
BH ₃ NH ₃ :hydroquinone:Rh (15:10:5)	7.773
BH ₃ NH ₃ :Polyaniline emeraldine (1:1)	10.556
BH ₃ NH ₃ :BZSM5:Ag/C (15:10:5)	11.273
BH ₃ NH ₃ :TiC:BZSM5 (2:1:1)	8.826
BH ₃ NH ₃ :Pyrene:PdCl(PPh ₃) ₂ (15:15:2)	8.266
BH ₃ NH ₃ :CoPYY/C:RhCl(PPh ₃) ₃ (15:15:2)	12.546
BH ₃ NH ₃ :CoPYY/C:V:RhCl(PPh ₃) ₃ (15:8:7:2)	12.059

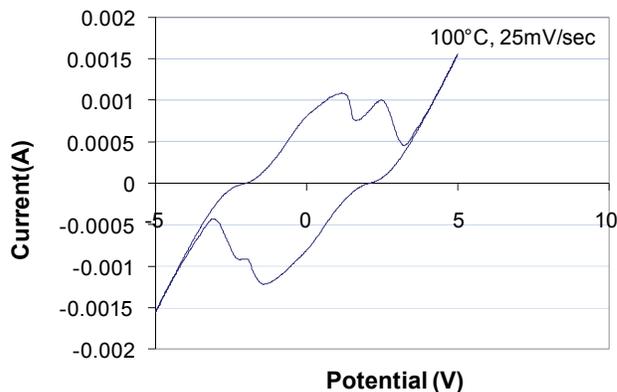


FIGURE 4. Cyclic Voltammetry of Boron-Nitrogen in Diglyme at 100°C

B. High Surface Carbon for Hydrogen Storage

The hydrogen storage electron-charge system is being developed under cooperation with the State University of New York (SUNY) at Syracuse. GTI tested eight samples provided by SUNY and the results are summarized in Table 3. The best hydrogen storage gravimetric capacity (Sample APKI-S6) is 7.0 wt% at 77 K.

TABLE 3. Summary of SUNY samples at 6,300 kPa

Sample Name	0°C (wt%)	77 K (wt%)
APKI-S6	0.58	6.38
APK25-N2	0.463	5.94
Ma015580-2	0	3.45
PZTAPK	0.39	5.47

Conclusions and Future Directions

- The electron charge experiments showed 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 also improves hydrogen charge/discharge kinetics. In situ regeneration of borane-nitride showed 75% increase in rate at 600 psig.

FY 2010 Publications/Presentations

1. A poster presentation on the overall project status was presented at the June 9, 2010 DOE Annual Merit Review Meeting in Washington D.C.

References

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