Ammonia-Borane Complex for H_2 Storage

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Start Date = September 2004

Planned Completion = September 2006

Rationale

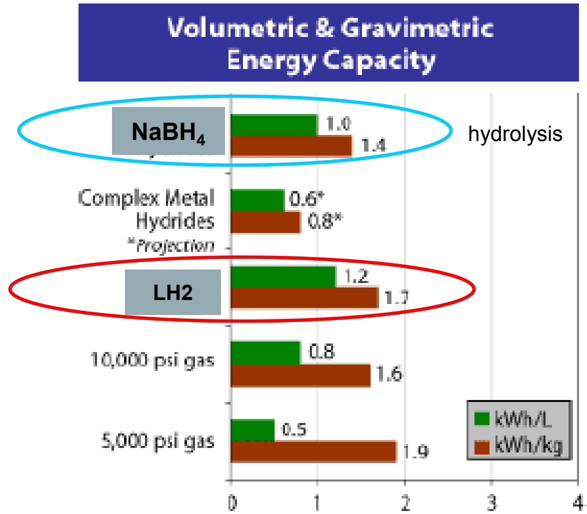
Reaction	Wt% H_2 Content	Capacity, Wh/kg
$LiBH_4 + 4H_2O \rightarrow LiOH + H_3BO_3 + 4\,H_2$	8.6	1,631
$NaBH_4 + 4H_2O \rightarrow NaOH + H_3BO_3 + 4\,H_2$	7.3	1,384
$NH_4F + LiBH_4 \rightarrow LiF + BN + 4\,H_2$	13.6	2,579
$NH_3BH_3 \rightarrow BN + 3\,H_2$	19.6	3,716
Lithium ion cell	N/A	130-150

Research Goals and Objectives

- Identify viable amine-borane (AB) complexes for hydrogen uptake & regeneration
- Develop a catalytic route for borazine hydrogenation to cyclotriborazane
- Study hydrogenation of polyborazylene
- Develop self-sustaining AB-based formulations
- Measure thermal conductivity of AB-based formulations

Relevance to Current State-of-the-Art

- 1 wt % H_2 = 0.19 kWh/kg
  (0.7 V; *i.e.* η_{FC} = 57%)
- Li ion cells: 0.**13 - 0.15** kWh/kg
- AB → BN + $3H_2$ (19.6 wt% H_2)
  (3.7 kWh/kg)



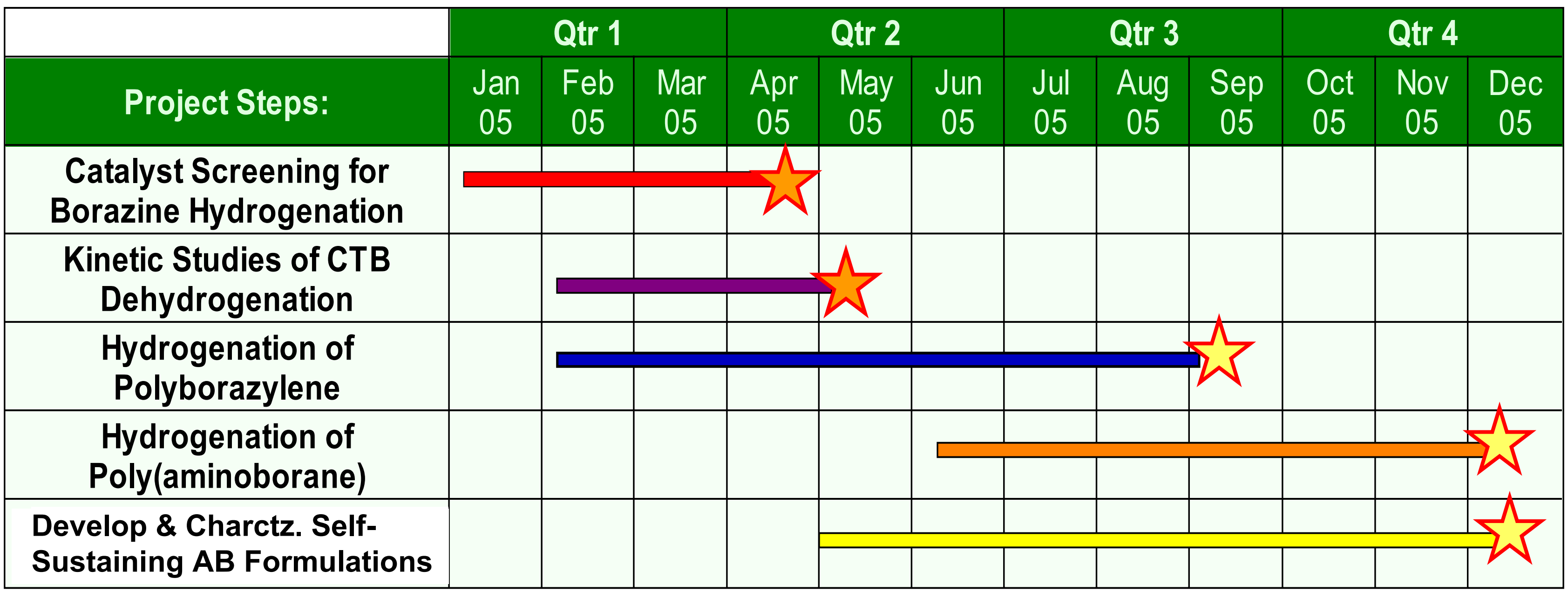
Credit: U.S. DOE-EERE-HFCIT

Relevance to NASA

- Ammonia borane complex provides high hydrogen storage capacity for **in-flight & LEAP** applications
- High energy density: 4.94 kWh/L for AB vs. 2.36 kWh/L for LH_2

Budget, Schedule & Deliverables

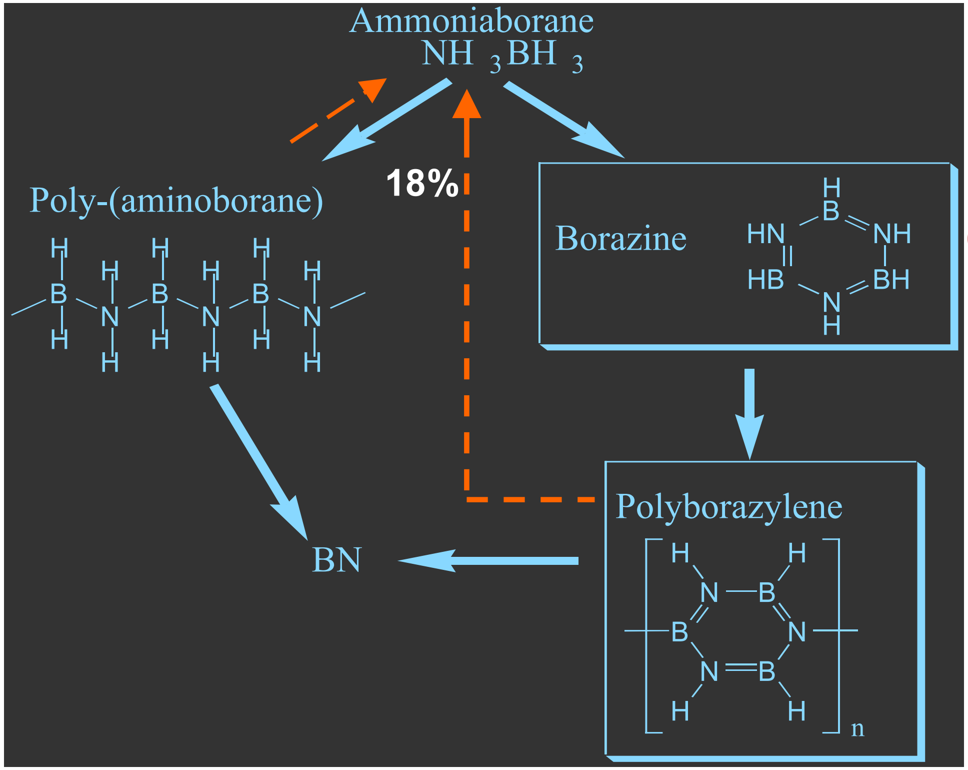
Fiscal Year 2005 Budget = $90k



Anticipated Technology End Use

- Development of AB-based energy storage devices that generate hydrogen gas quickly and safely without a requirement for the external energy input & without the generation of undesirable gas-phase decomposition products such as borazine that adversely affect the operation of PEMFCs.
- If successful, a AB-based hydrogen storage device having a system-level specific energy density of 1 kWh/kg or better will be fabricated and tested at FSEC. Such a system if of immense interest to the U.S. DOE (stationary as well as the vehicular H_2 storage applications) & DOD (for soldier portable power source, among others).
- DOE & DOD request for proposals are streaming out of the Agencies and contain R&D topics related to better and safer means of hydrogen storage & use.

NH_3BH_3 (AB) Pyrolytic Routes



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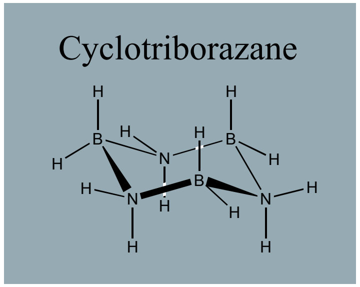


Accomplishments & Results

- Conducted catalyst screening of borazine hydrogenation.
- Investigated polyborazylene reduction mechanism.
- Adsorbed species on the surface of the borazine treated with 5% Rh catalyst were stable up to 120°C suggesting that during catalytic hydrogenation of borazine at room temperature & below, borazine is stable.
- Solvent-free hydrogenation of polyborazylene was accomplished & the level of hydrogenation achieved was in the range of 15%-16.5%.
- Several self-sustaining AB formulations were developed & tested.
- For the first time ever, the thermal conductivity of AB complex & its solid-state decomposition products were measured in a wide range of temperatures.

Accomplishments & Results

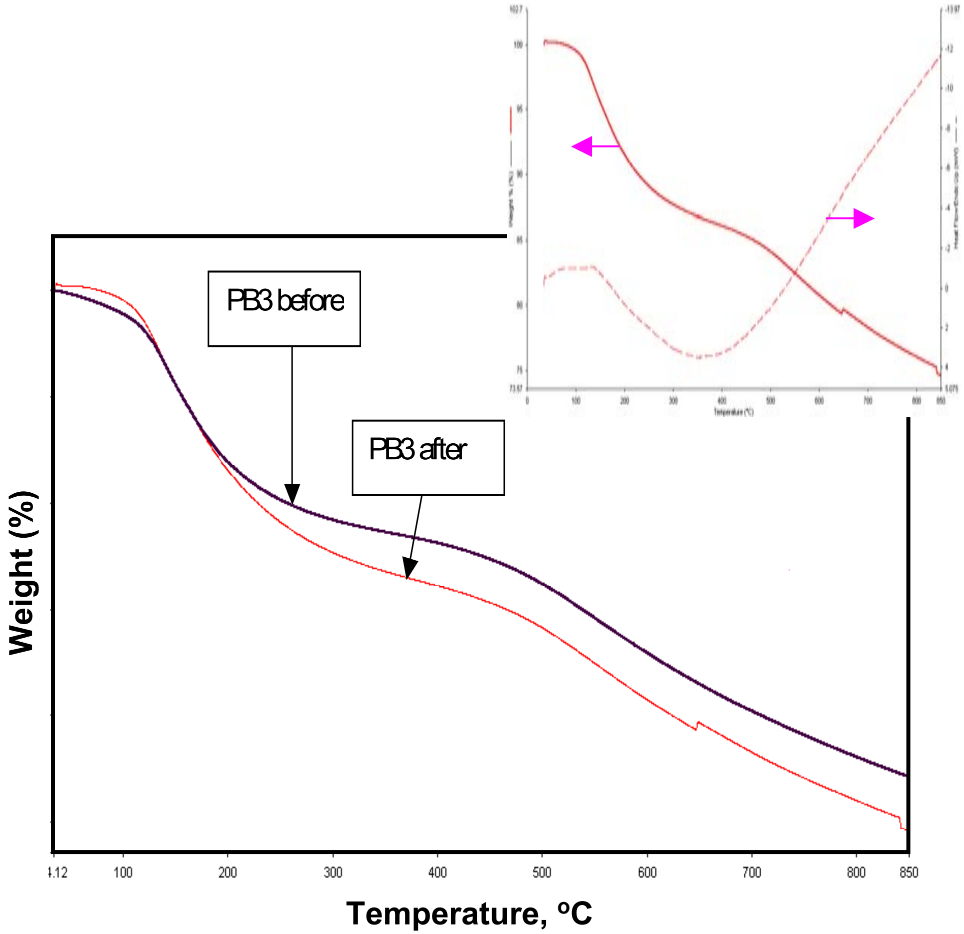
Solvent-free hydrogenation of polyborazylene

Sample	Composition	H_2 Pressure (psi)	Hydrogenation period (hrs)
PB1	PB (0.2 g) - 5% Pd on $BaCO_3$ (2 mg)	250	12
PB2	Same as above	1010	24
PB3	PB (0.2 g) - 5% Rh on C (2 mg)	250	12

Sample	Percent Weight Loss at 850 °C		Extent of Hydrogenation %
	Before Hydrogenation	After Hydrogenation	
PB1	19.27	21.81	**2.54**
PB2	19.27	21.65	**2.38**
PB3	22.83	25.38	**2.55**

TG Curves for PB3 Before & After Hydrogenation

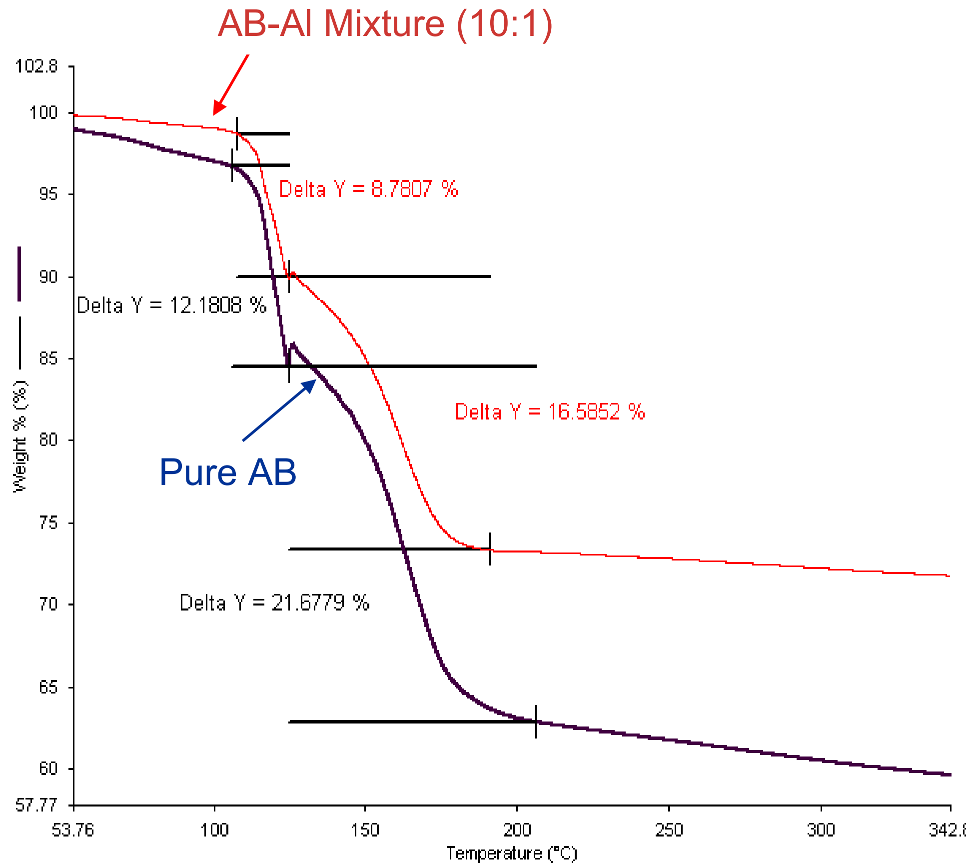
- The weight changes were associated with the exothermic dehydrogenation region of TG curves.
- Independent of catalysts or H_2 gas pressure used in this study.



Self-Sustaining AB-Based AB Formulations TG Analysis

- Addition of Al powder to AB complex <u>decreases</u> mass loss due to release of undesirable thermolysis products such as borazine, diborane & Ammonia

- H_2 release efficiency was <u>facilitated</u> by addition of aluminum powder to AB complex



Self-Sustaining AB Thermolysis

- AB thermolysis is exothermic with ΔH_r = -(21.7 $\pm$ 1.2)kJ/mol*
- C_p of AB complex @ 298K = 75.37 $Jmol^{-1}K^{-1}$**
- Thermal decomposition of AB starts at ~ 110 °C
- Activation energy necessary to reach this temperature:

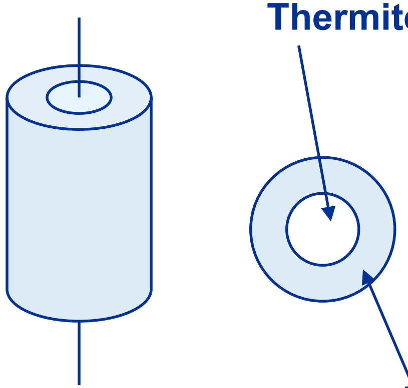
  Q_{act} = Cp * ΔT = 75.37 x 85 = 6.41 kJ/mol
- Thermite reaction: $Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$

  ΔH_r = 851.7 kJ/mol
- Theoretical molar ratios of AB:Fe_2O_3:Al to be mixed to reach the decomposition temperature of one mole (30.8g) AB complex are 1:0.0075:0.015.

* G. Wolf, et al. *Thermochimica Acta* 343 (2000) 19-25.

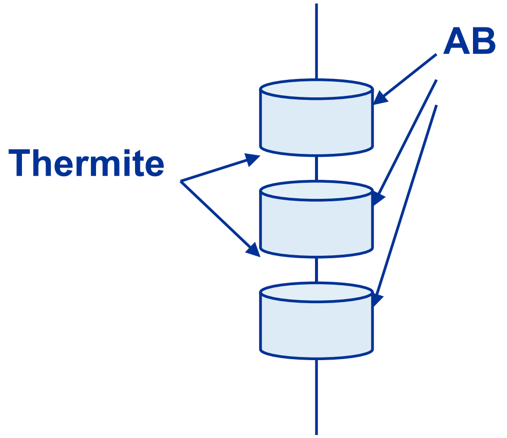
** G. Wolf, et al. *Thermochimica Acta 317 (1998) 111-6.*

Self-Sustaining AB Thermolysis, *cont'd*



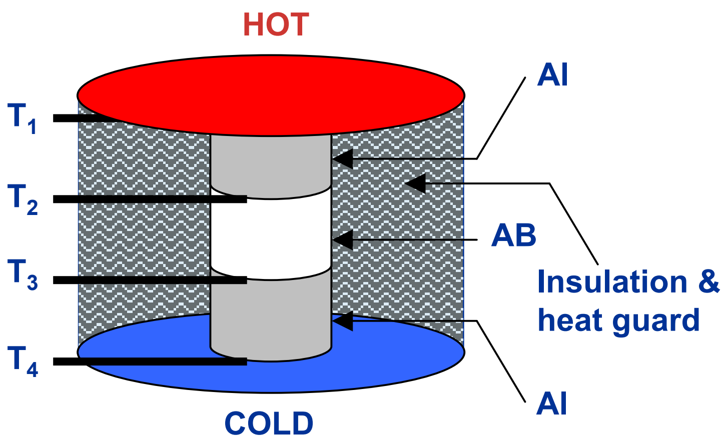
- AB = 0.24 g
- Thermite = 0.04g (4 times more than theoretical quantity needed).
- Thermolysis using NiCr wire produced 380 mL of gas (If all H_2, then 72% of theoretical value).
- Was not self-sustaining.
- GC/MS analysis of the gas showed a mixture of H_2 & borazine. Also, poly(aminoborane) was reaction product.

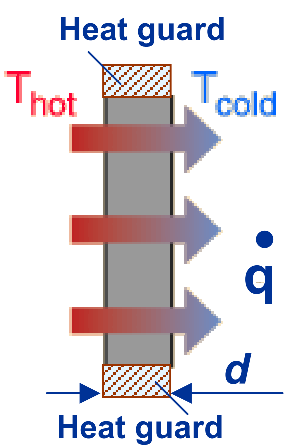
Self-Sustaining AB Thermolysis, *cont'd*



- AB = 0.338 g.
- Thermite = 0.1g (6 times more than theoretical amount required).
- Thermolysis using NiCr wire produced 510 ml of gas (If all Hydrogen then 69% of theoretical value).
- Was self-sustaining.
- Amount of borazine & Poly(aminoborane) increased.

Thermal Conductivity Measurements



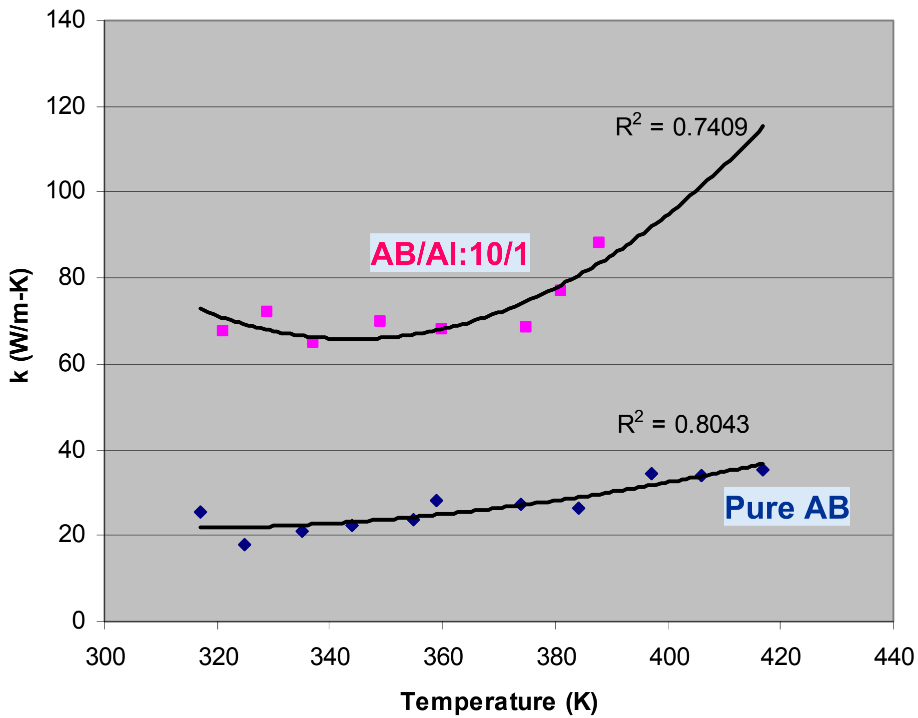


- Reference:
  - Aluminum 6061-T6 alloy
  - $k = 180\ \mathrm{Wm^{-1}K^{-1}}$
  - Cylinder with OD = 0.378” & h = 0.181”
- The AB pellets (same dimensions as the Al cylinders) were placed in between two identical Al cylinders
- Temperature measurements were made using four T-type thermocouples

$$\dot{q} = k\,\frac{(T_{HOT}-T_{COLD})}{d}$$

Thermal Conductivity of Pure AB & AB mixed with Al (10:1)

- Thermal conductivity of pure AB complex is close to that of the dielectric materials:
  - $k_{\text{AB Complex}} \approx 20$ W/m-K
  - $k_{\text{Alumina}} =$ 30 W/m-K
  - $k_{\text{Calcium Oxide}} = 16$ W/m-K
- Apparent AB thermal conductivity increases by 3 folds when 10% by weight of Aluminum powder was added.



Future Plans

- Develop a more efficient method for the polyborazylene hydrogenation.
- Find an improved method for poly(aminoborane) hydrogenation.
- Develop new & improved AB formulation(s) that lend themselves to "self-sustaining" pyrolytic reactions that generate hydrogen gas quickly and safely without external energy input & without the production of undesirable gas-phase decomposition products such as borazine.
- Fabricate a AB-based hydrogen storage device having a system-level specific energy density of 1 kWh/kg or better.

Publications & Proposal Activities

- *"Regeneration of Ammonia-Borane Complexes for Hydrogen Storage,"* Nahid Mohajeri and Ali T-Raissi, *Proc. 2005 MRS Spring Meeting*, San Francisco, CA, March 28-April 1, 2005.
- "Regeneration of Amineborane Complexes for On-board Hydrogen Storage," an FSEC proposal to the U.S. DOE, Basic Energy Sciences, Solicitation No. DE-FG01-04ER04-20, Jan. 2005, $1,143,639. Status: <u>not funded</u>.
- "A Compact Borazane Hydrogen Generator for a Soldier Fuel Cell Power System," a joint E & S Consulting, Inc. and FSEC proposal submitted under DOD SBIR/STTR Topic No. A05-034, July 15, 2005, $120,000. Status: <u>pending</u>.

Thank You

Questions?