Complex Hydrides for Hydrogen Storage

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Efficient onboard hydrogen storage is a critical enabling technology for the use of hydrogen in vehicles

- The low volumetric density of gaseous fuels requires a storage method which densifies the fuel.
  - This is particularly true for hydrogen because of its lower energy density relative to hydrocarbon fuels.
- Storage methods result in additional weight and volume above that of the fuel.

How do we achieve adequate stored energy in an efficient, safe and cost-effective system?

One storage option is to chemically bond hydrogen in a solid material

- This storage approach should have the highest hydrogen packing density.

However, the storage media must meet certain requirements:

- reversible hydrogen uptake/release
- lightweight
- low cost
- cyclic stability
- rapid kinetic properties
- equilibrium properties (P,T) consistent with near ambient conditions.

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Where do we start?

Period / Group

Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB	-------	VIII	-----	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.47	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 190.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac~ (227)													116 --- ()		118 --- ()

Series														
Lanthanide Series*	58 Ce 140.1													71 Lu 175.0
Actinide Series~	90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

The online data base
hydpark.ca.sandia.gov
lists over 2000 elements, compounds and alloys that form hydrides.

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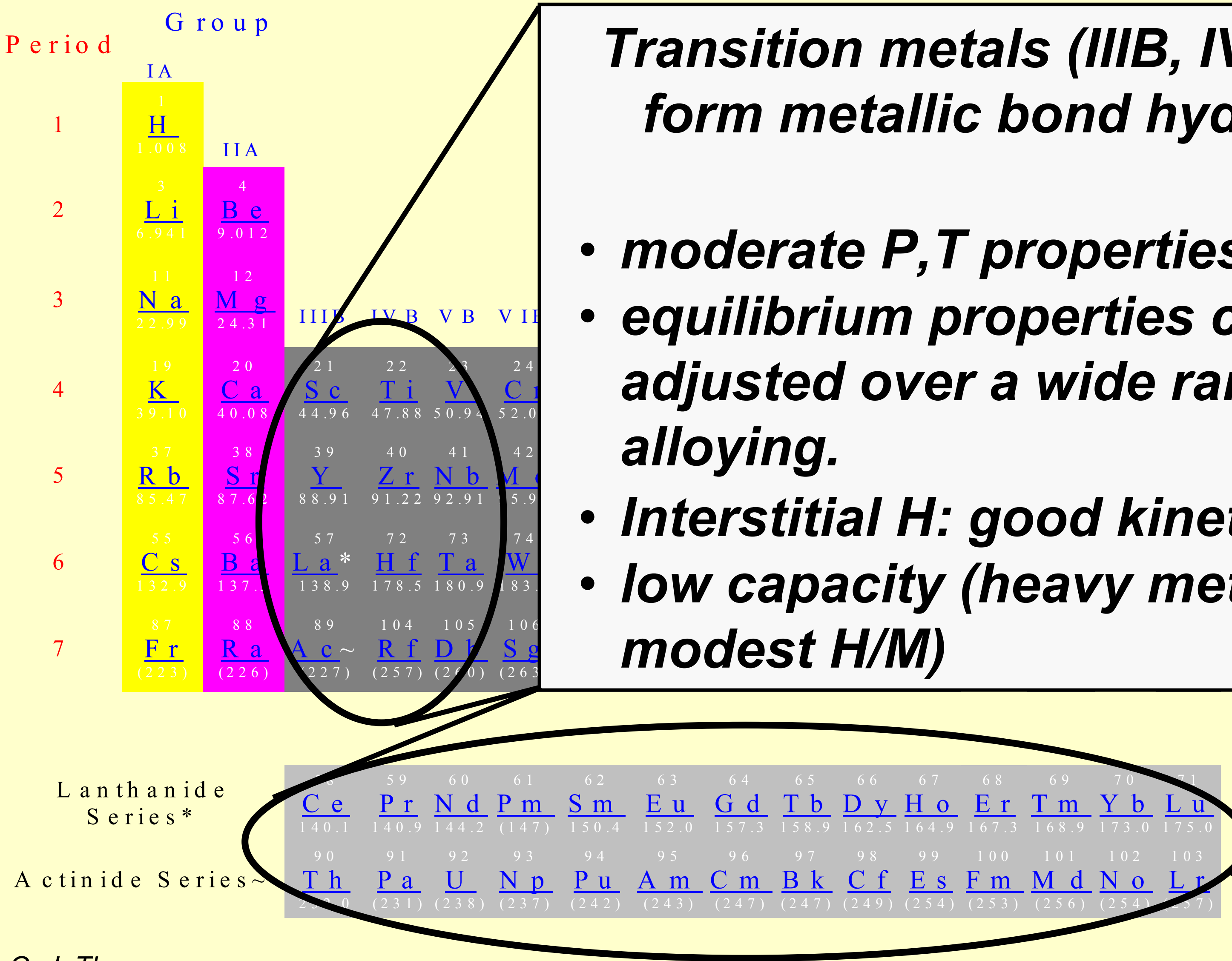
Where do we start?



Transition metals (IIIB, IVB, VB) form metallic bond hydrides

- ***moderate P,T properties***
- ***equilibrium properties can be adjusted over a wide range by alloying.***
- ***Interstitial H: good kinetics***
- ***low capacity (heavy metals, modest H/M)***

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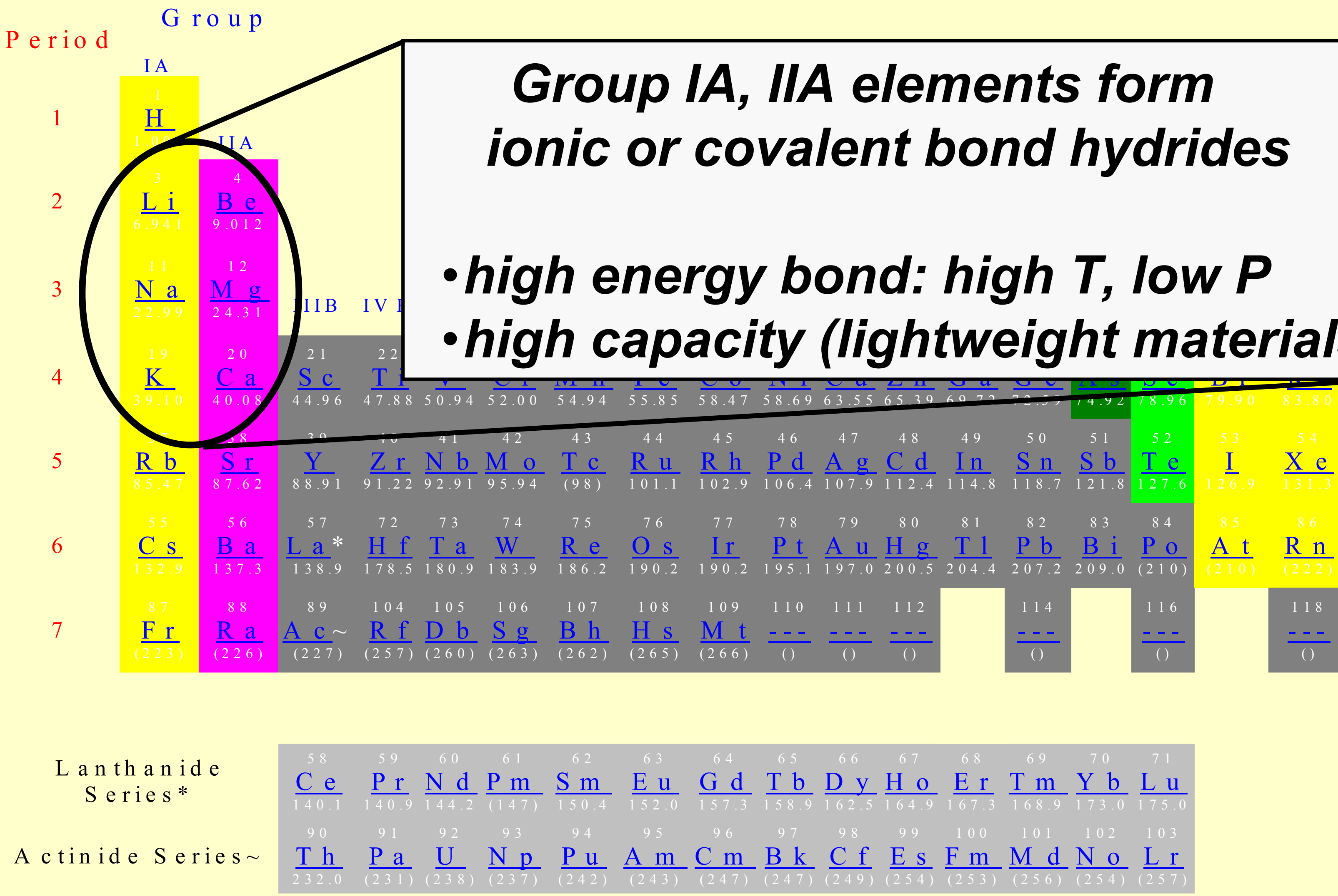
Where do we start?



Group IA, IIA elements form ionic or covalent bond hydrides

- ***high energy bond: high T, low P***
- ***high capacity (lightweight materials)***

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Where do we start?

Hydrogen can also form complexes with some elements

Group

Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
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7	87 Fr (223)	88 Ra (226)	89 Ac~ (227)	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 --- ()	111 --- ()	112 --- ()		114 --- ()		116 --- ()		118 --- ()

Series														
Lanthanide Series*	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
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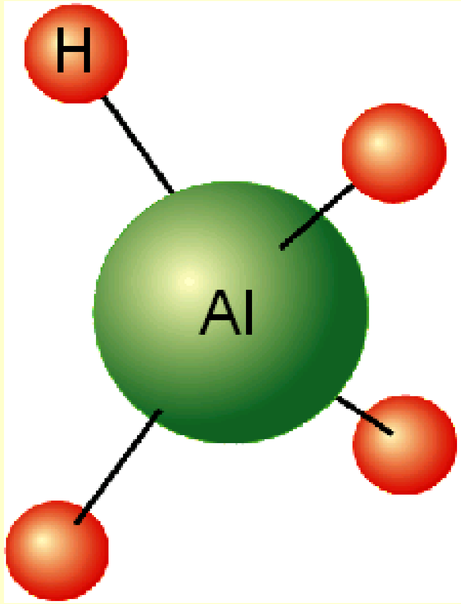
Complex hydrides give you another "knob to twist"

- Complex hydrides consist of a **H=M** complex with additional bonding element(s)
- hydrogen complexes include:
  - **$(AlH_4)^-$** (alanates)
  - **$(BH_4)^-$**
  - with Group VIII elements
- features:
  - ionic, covalent, metallic bonding
  - can have lower formation energy
  - can have high H/M
- 173 complex hydrides listed on *hydpark.ca.sandia.gov*



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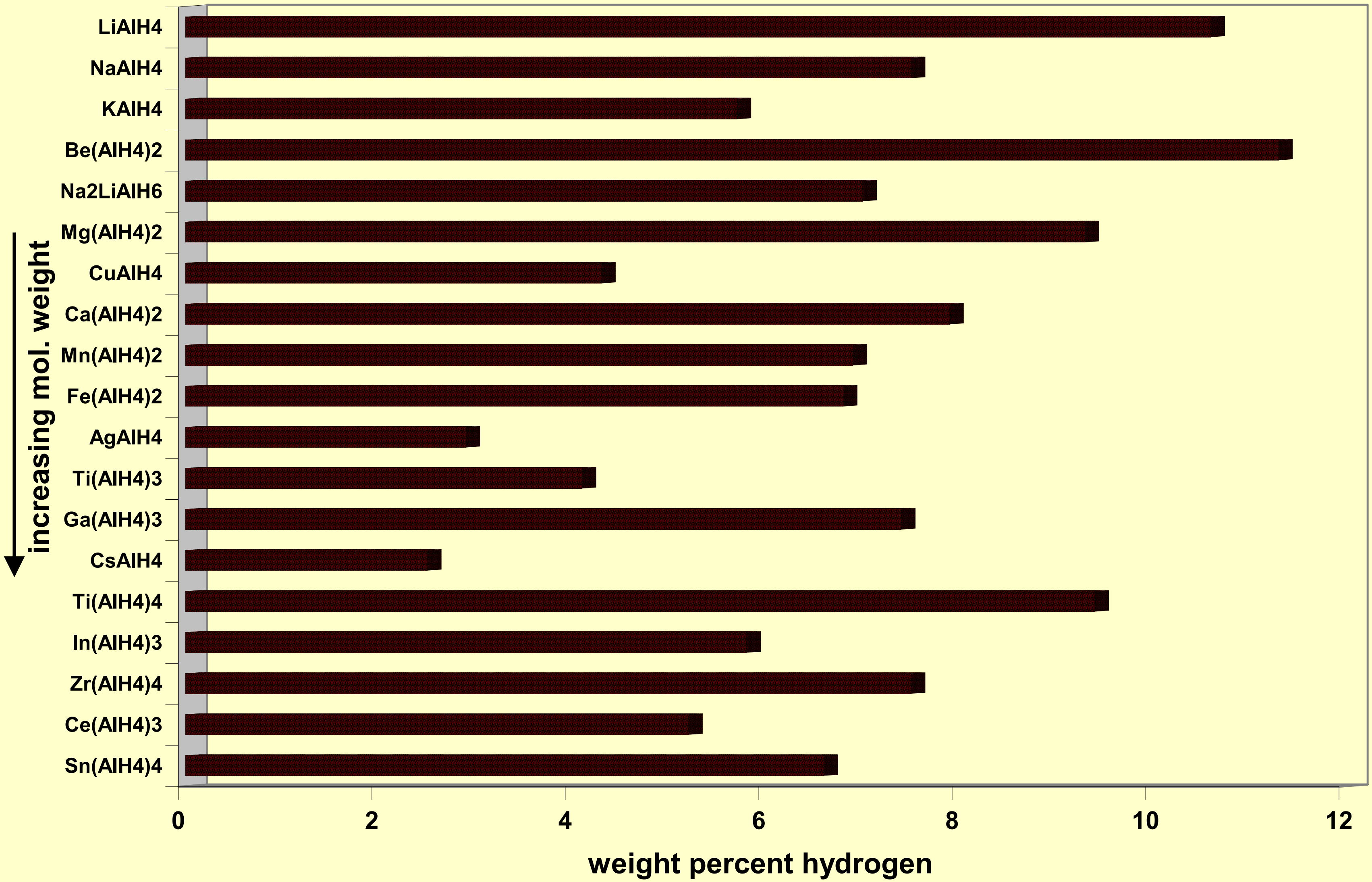
Total hydrogen content of some alanates



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Issues with complex hydrides

- Reversibility
  - role of catalyst or dopant
- Thermodynamics
  - pressure, temperature
- Kinetics
  - long-range transport of heavy species
- Cyclic stability
- Synthesis
- Compatibility/safety

only $NaAlH_4$ has been studied in detail to date
this material serves as a model system to better understand other complex hydrides

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Brief history of $NaAlH_4$

- Compound first reported by Finholt & Schlesinger in 1955
- Direct synthesis developed by Ashby (1958) and Clasen (1961)
- Principal use has been as a chemical reducing agent
- There have been numerous characterization studies: (Dymova, Zakharkin, Claudy, Wiberg...)
- Reversibility demonstrated by use of Ti catalyst (Bogdanovic and Schwickardi MH96, JAC 253(1997) 1)

this development spurred renewed interest in using complex hydrides as storage materials

Na Alanate - a reversible complex hydride

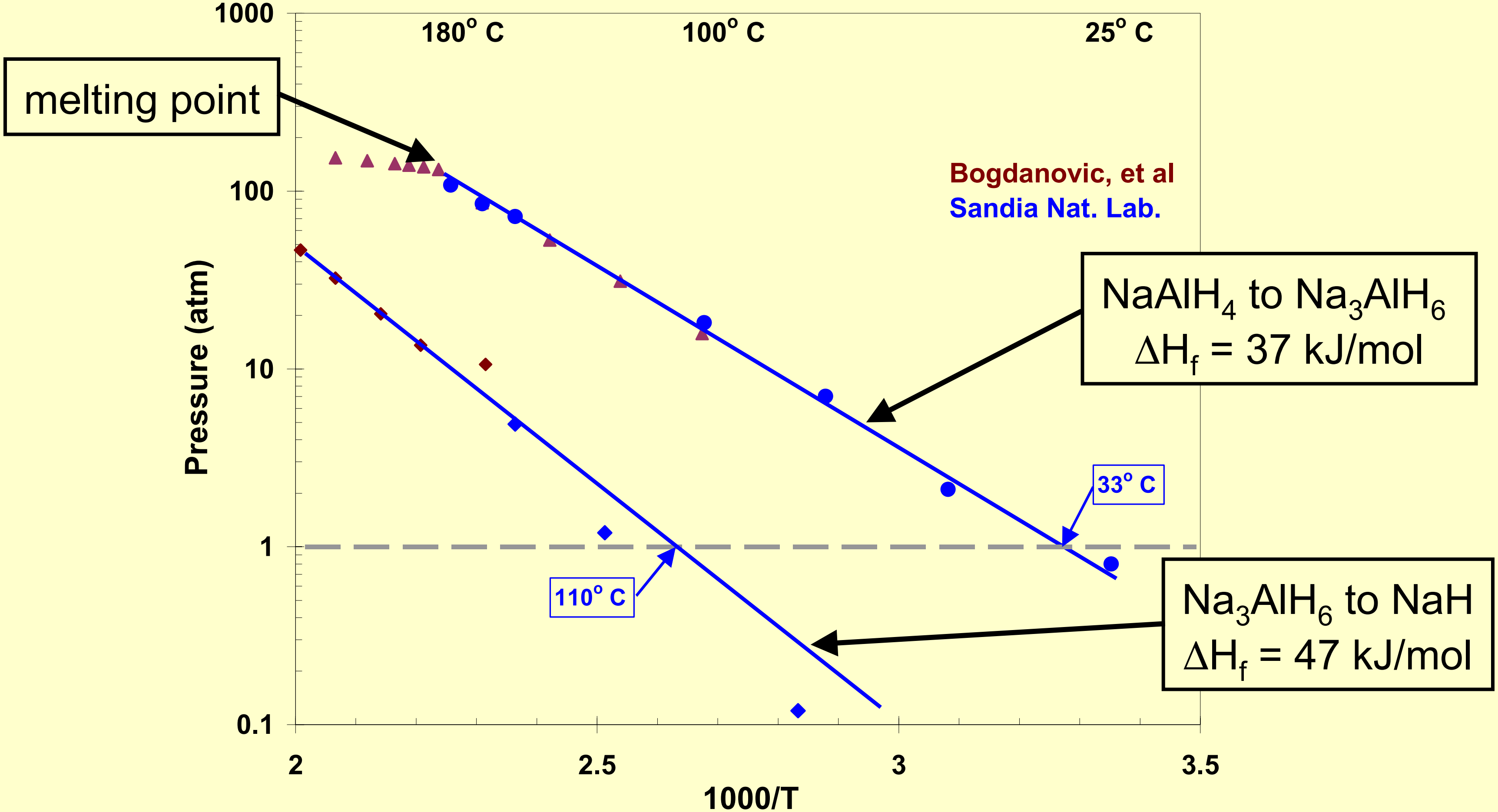
- There are five labs within USDOE program during FY02 working on complex-based hydrides, focused mainly on $NaAlH_4$
  - Univ. of Hawaii — Prof. C. Jensen
  - Sandia Nat. Lab. — Dr. K. Gross
  - Florida Solar Energy Center — Dr. D. Slattery
  - United Tech. Res. Center — Dr. D. Anton
  - Savannah River Tech. Center — Dr. R. Zidan
- These labs have formed a working group to corrdinate their activities and share information.

Na Alanate - a reversible complex hydride

- There are development projects outside of the US.
  - B. Bogdanovic, Max Planck Inst., Mulheim, Germany
    - GM Opel support
  - A. Zaluska, L. Zaluski
    - recently left McGill Univ. (Canada)
    - HERA (HydroQuebec, GfE, ShellHydrogen)
  - Japan funding development through WENET, AIST
- Ames Laboratory has recently published some work on Li alanate

Thermodynamic data

$$3NaAlH_4 \xleftrightarrow{catalyst} Na_3AlH_6 + 2Al + 3H_2 \xleftrightarrow{catalyst} 3NaH + Al + 3/2H_2$$



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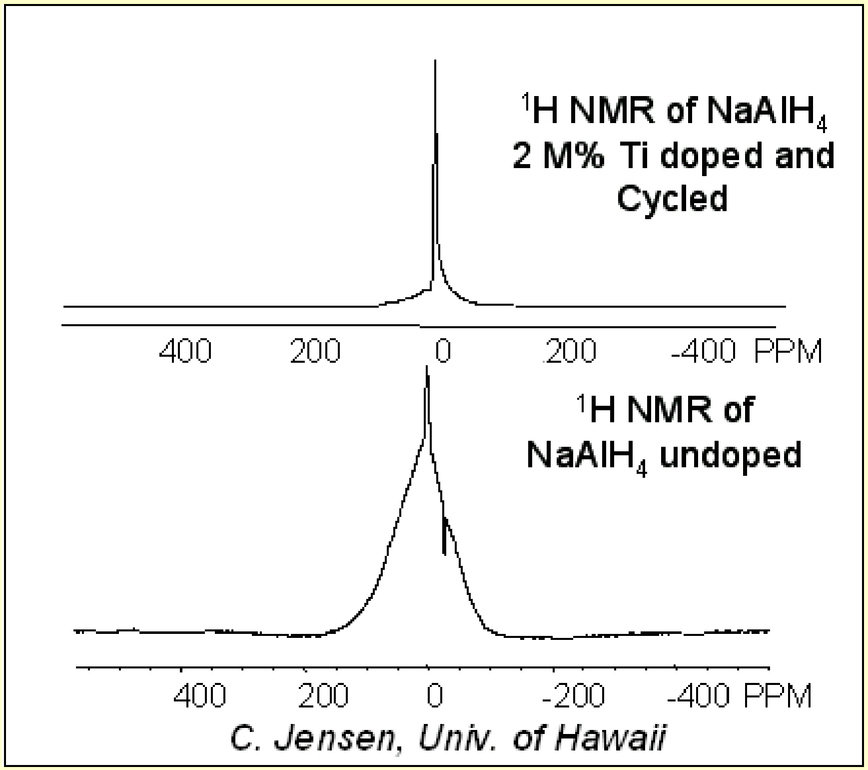
Current studies on $NaAlH_4$

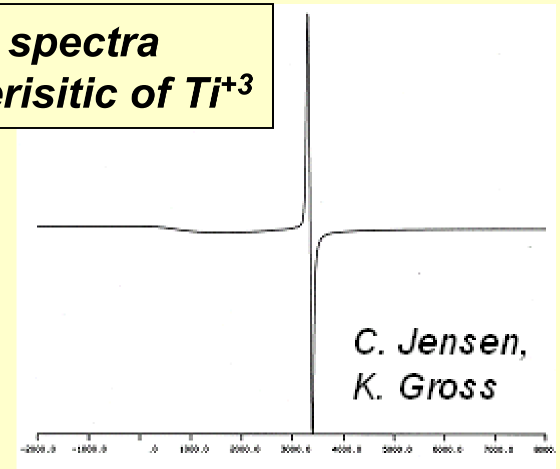
- Mechanisms
  - experimental
  - modelling
- catalysts, doping
- mechanical processing
- synthesis
- engineering properties

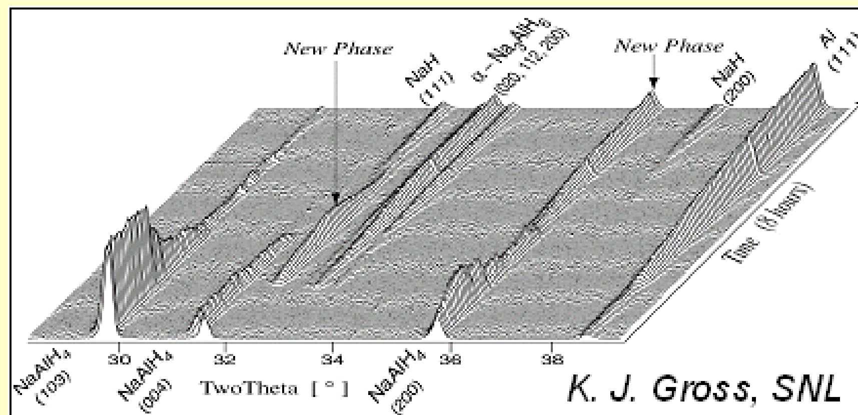
Understanding $NaAlH_4$ mechanisms will help in developing higher capacity hydrides

NMR shows Ti doping enhances proton mobility



ESR spectra characterisitic of Ti^{+3}





Decomposition of undoped $NaAlH_4$

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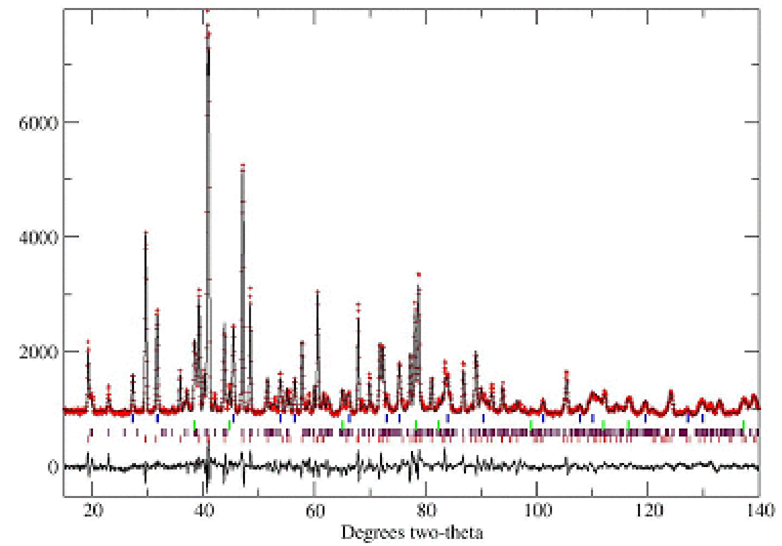
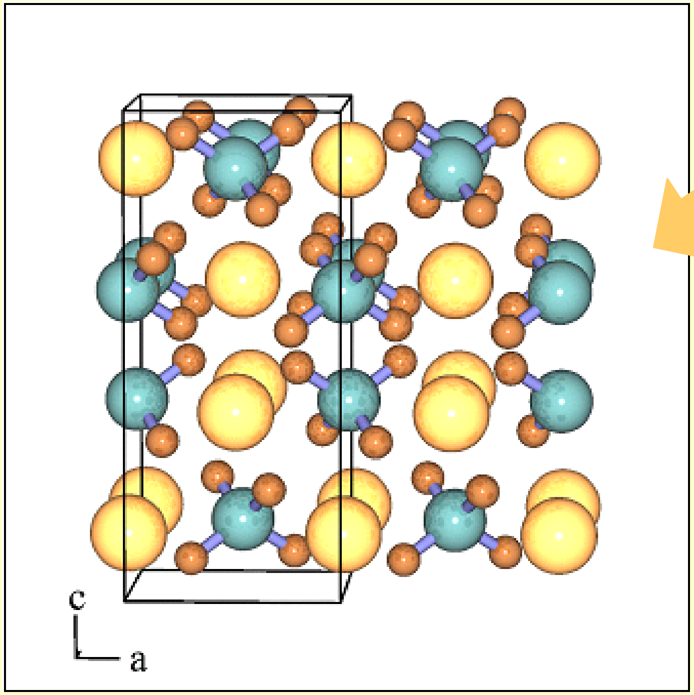
Crystal structure and modeling

Neutron diffraction
Rietveld refinement



E. Majzoub, SNL



Ab initio **calculations using VASP**

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Catalysts/Doping

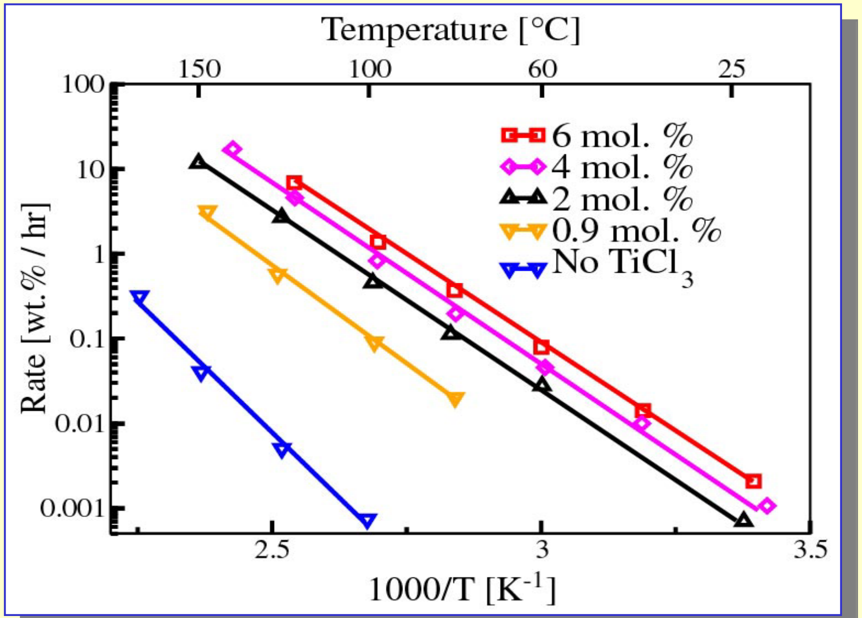
- Initially, reversibility believed due to catalytic effects.
  recent evidence, however, indicates bulk doping.
- 3 factors affect hydride performance:
  (1) catalyst/dopant
    - numerous compounds evaluated.
    - Ti-based most effective.

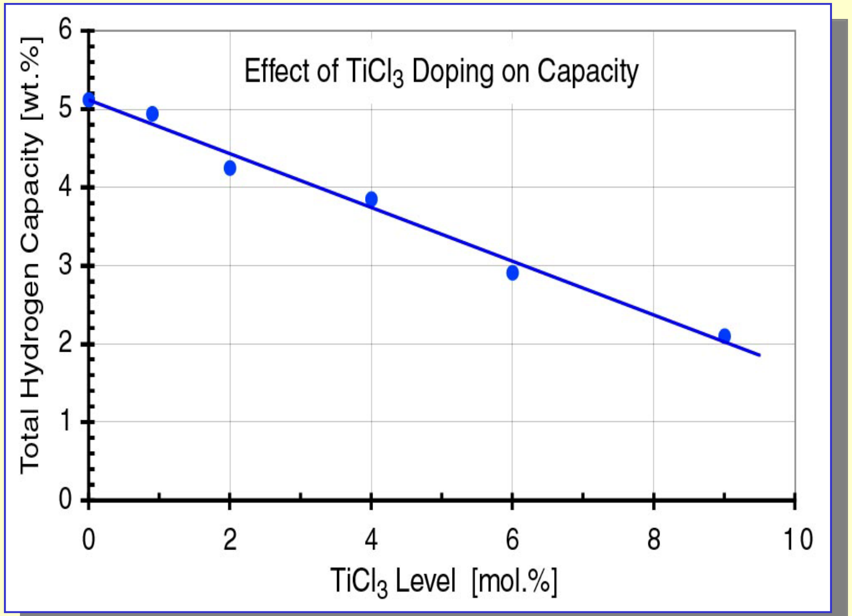
  (2) method of introduction
    - mechanical mixing (dry process)
    - wet chemistry
    - precursor must react with alanate

  (3) amount of catalyst/dopant

Catalyst/Doping level affects kinetics and capacity

$NaAlH_4$





(G. Sandrock, K. J. Gross, G. Thomas, JAC 339 (2002) 299)

- ***Initial kinetics exhibit Arrhenius behavior***
- ***different activiation energy in doped material***
- ***activation energy constant for 2 mol% and greater doping***
- ***faster kinetics with higher doping levels***

- ***Trade-off between faster kinetics and loss of capacity with increasing doping levels***

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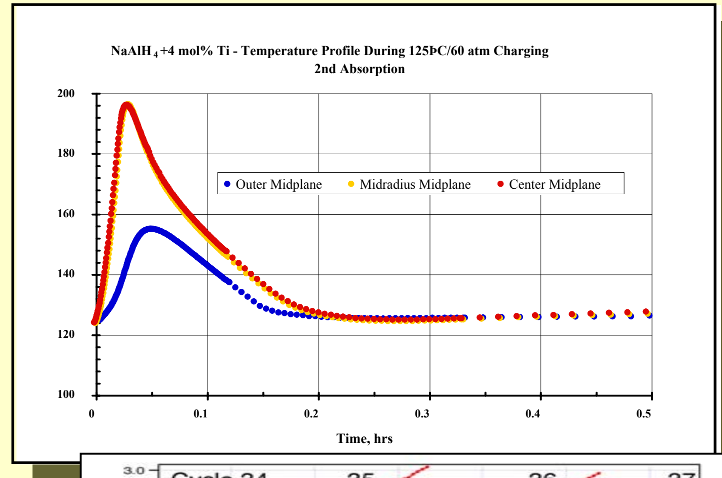
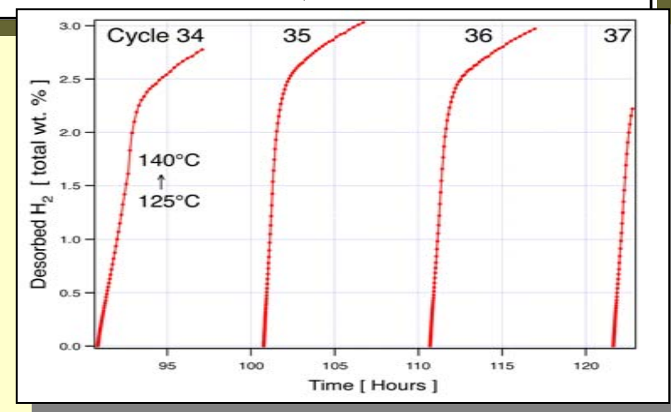
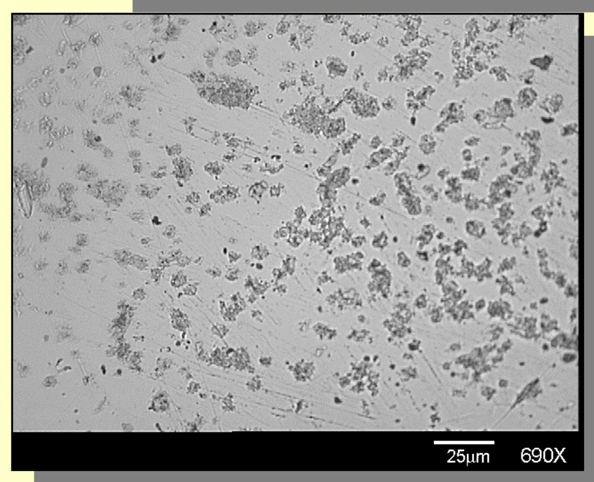
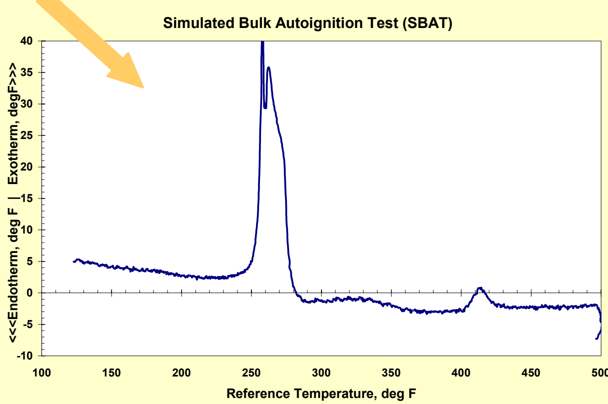
Engineering Properties

- Thermal conductivity
  - similar to IM hydrides cycling
  - stable to ~100 cycles
- material compatibility
  - no issues with Al, SS
- safety
  - sensitive to impact, thermal environment with air exposure.









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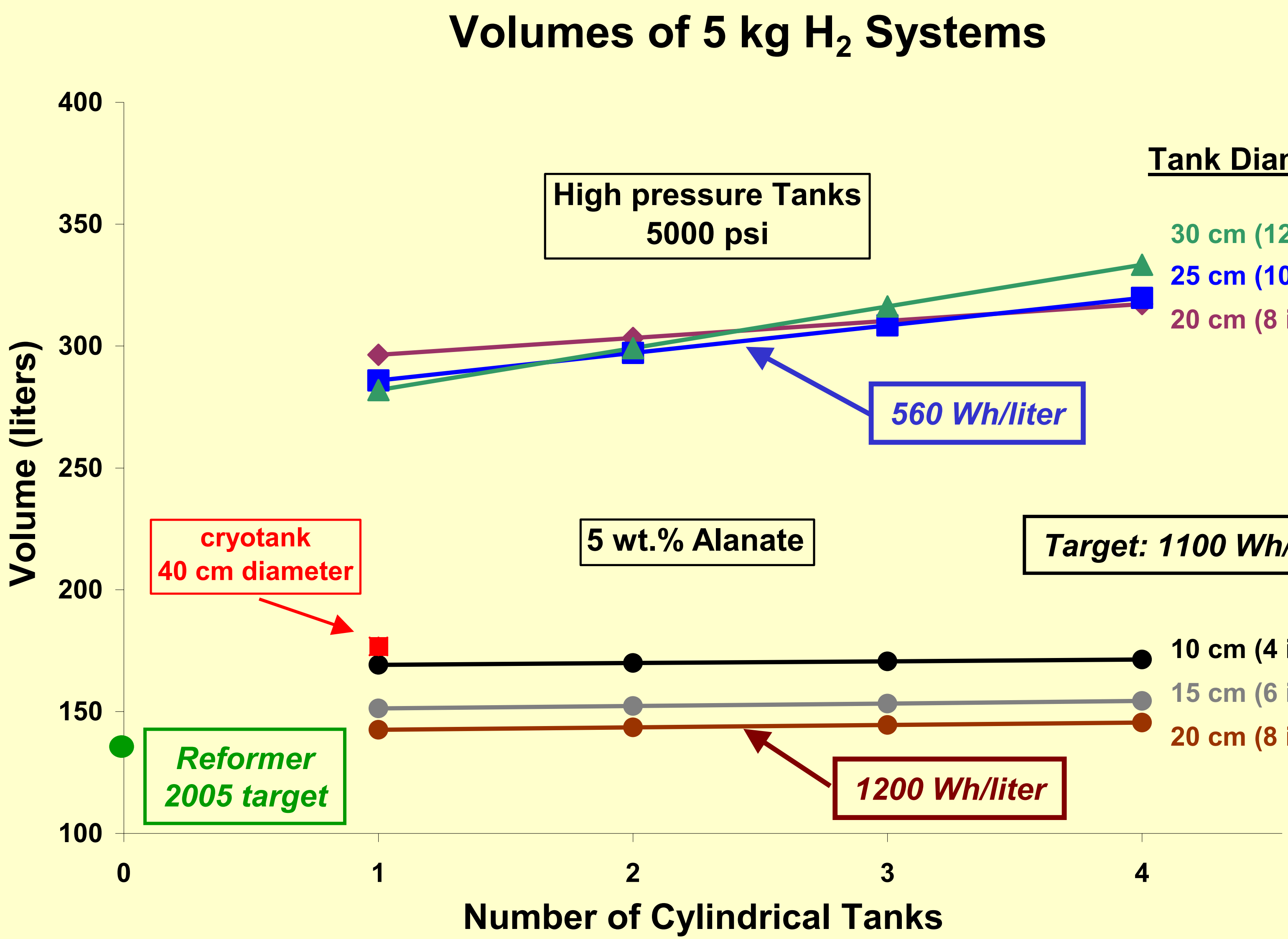
5 kg H_2 system volumes



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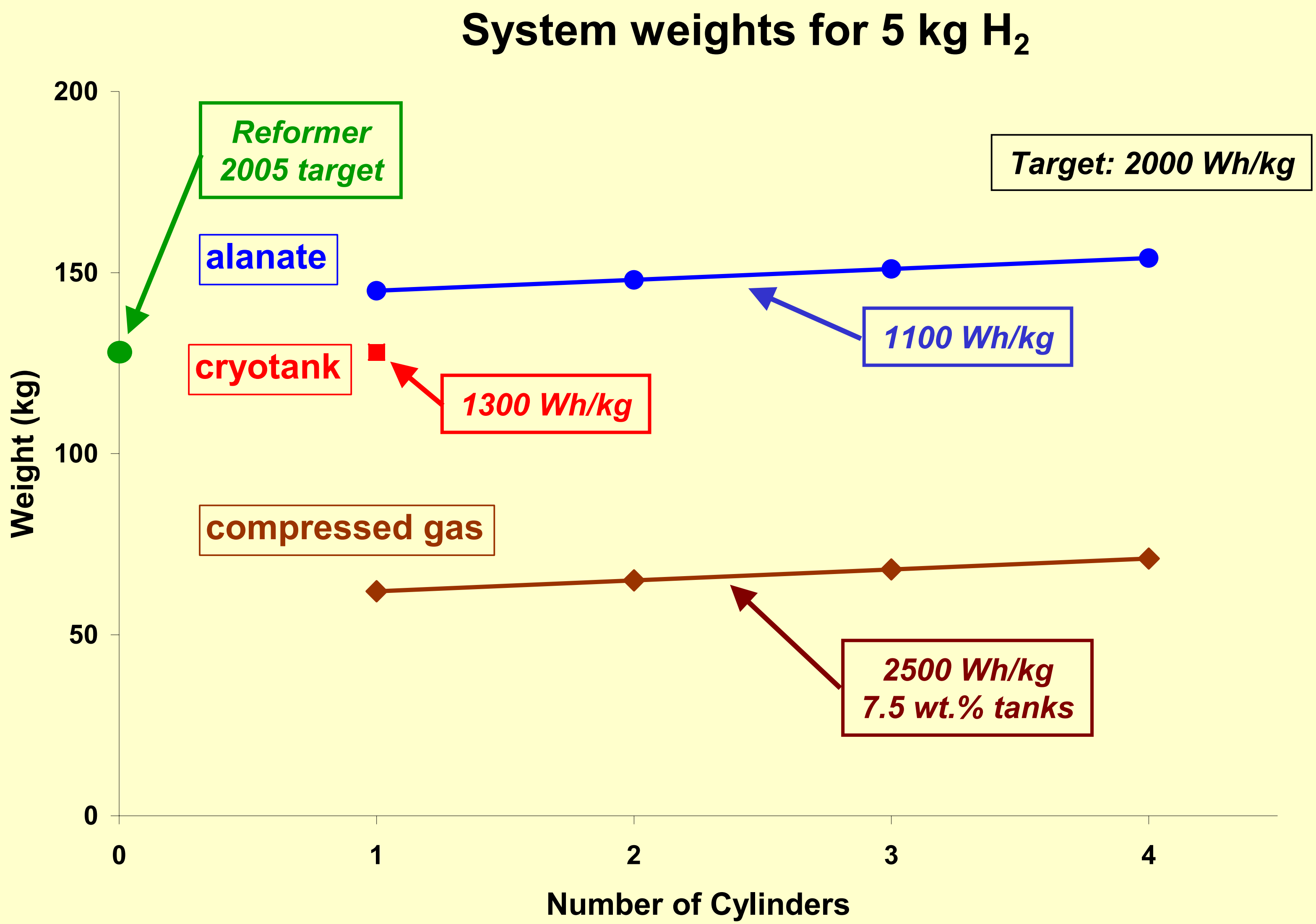
5 kg H_2 system weights



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A complex hydride based on BH_4^- forms the basis for a chemical hydride storage system

- Development efforts largely financed privately.
  - Millenium Cell
    an IP company with no plans to manufacture.
  - Kogakuin Univ., Japan (Prof. S. Suda)
- Both based on borohydride chemistry.
  - each use different catalyst.
- System has 4-10 wt.% capacity
- reversibility a problem with boron-based systems

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 + heat$$

20 - 35% sol. Stabilized with 1-3% NaOH

Proprietary catalyst

Borax in NaOH

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Where do we go from here?

- What's beyond $NaAlH_4$?
  - Capacity appears limited to ~5 wt.%
  - modifications or new complexes needed.
- Some improvements in weight, volume and cost can be realized by better container engineering.

Intermetallic hydrides were studied for thirty years before doped alanates provided a significant improvement in capacity.

We need to be a little faster!