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.

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 --- ()

Lanthanide Series*	58 Ce 140.1												b 0	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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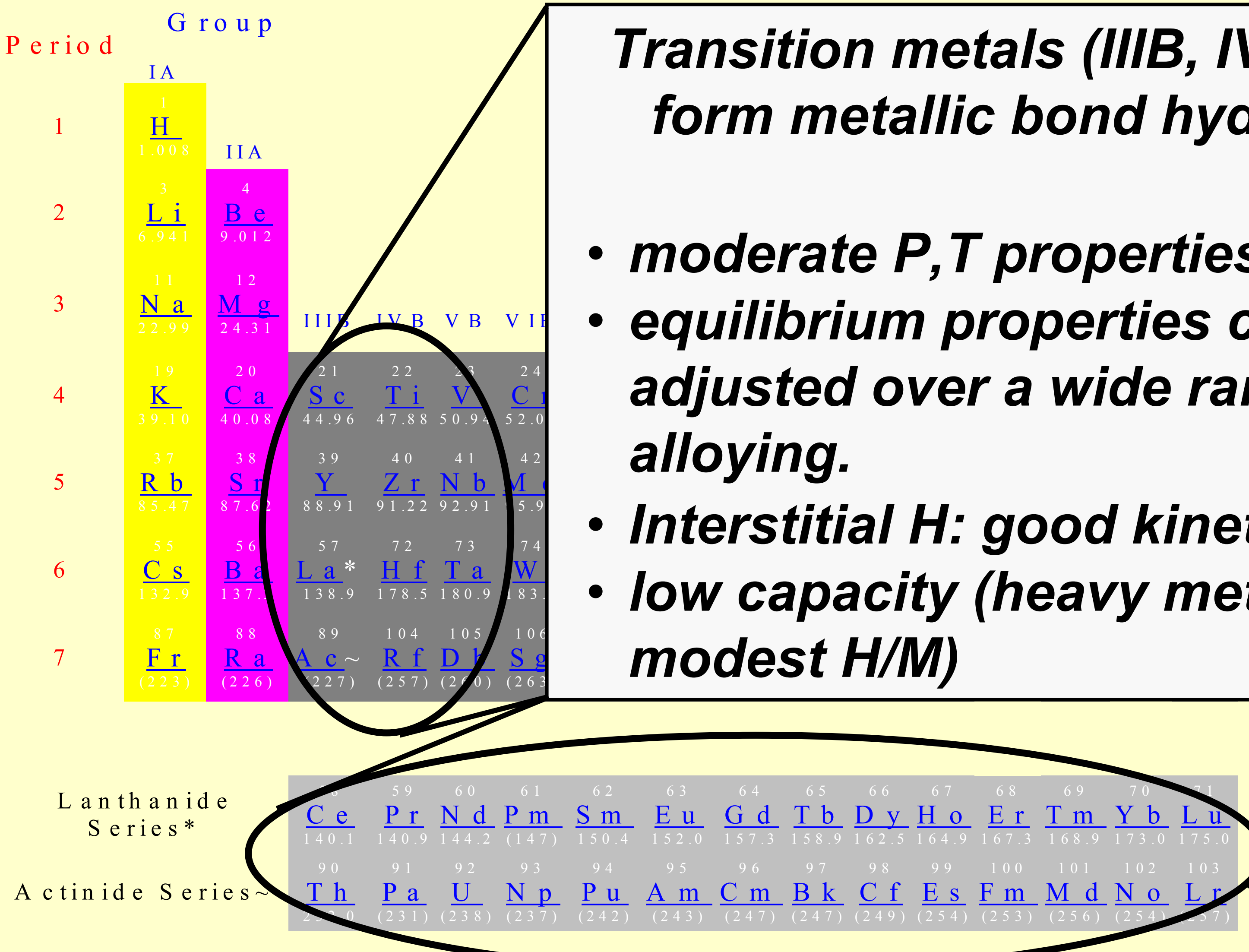
Where do we start?



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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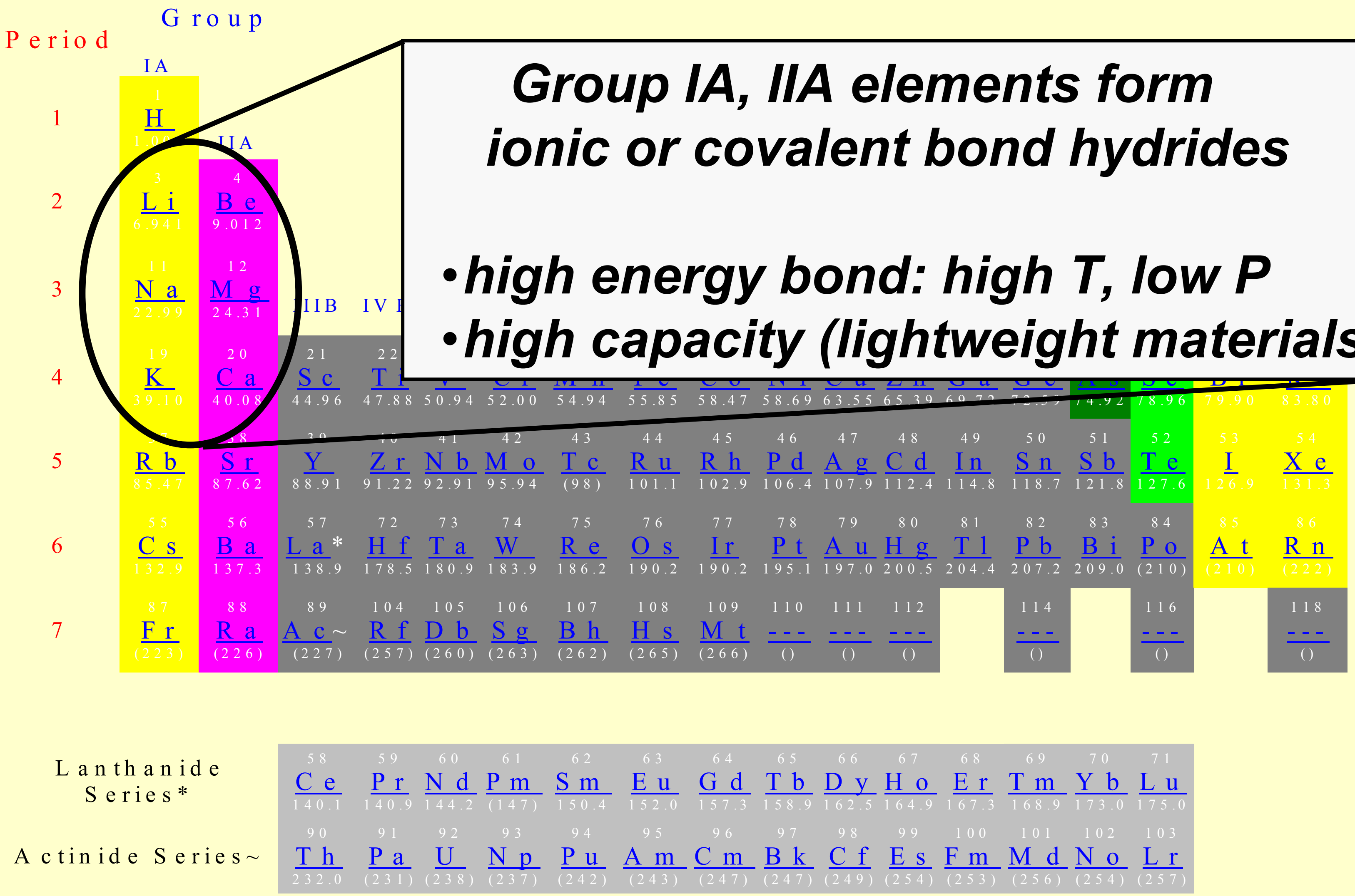
Where do we start?



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

			IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
																		2 He 4.003
2	Li 6.941	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
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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 --- ()

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
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)

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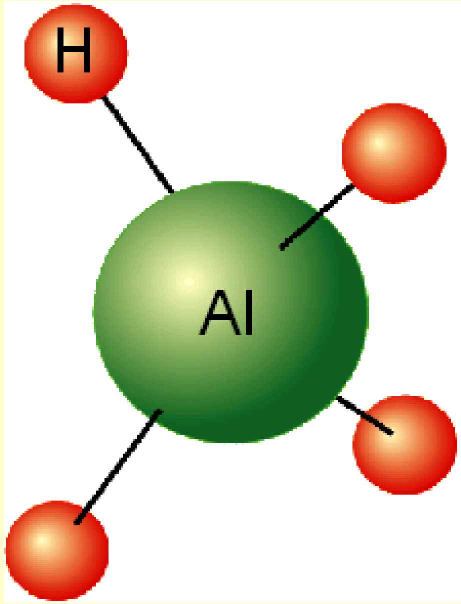
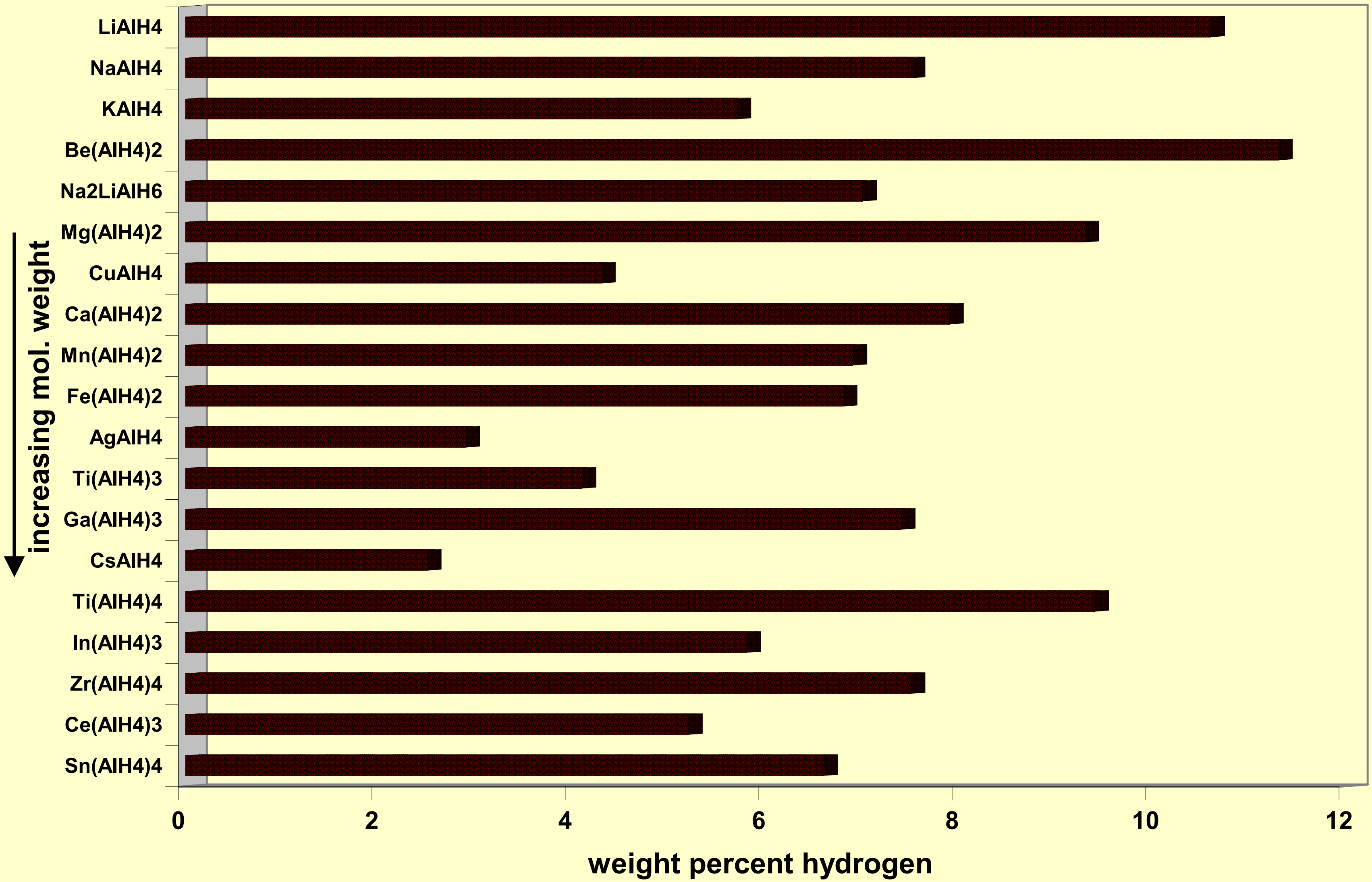
Complex hydrides give you another "knob to twist"

- 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*



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

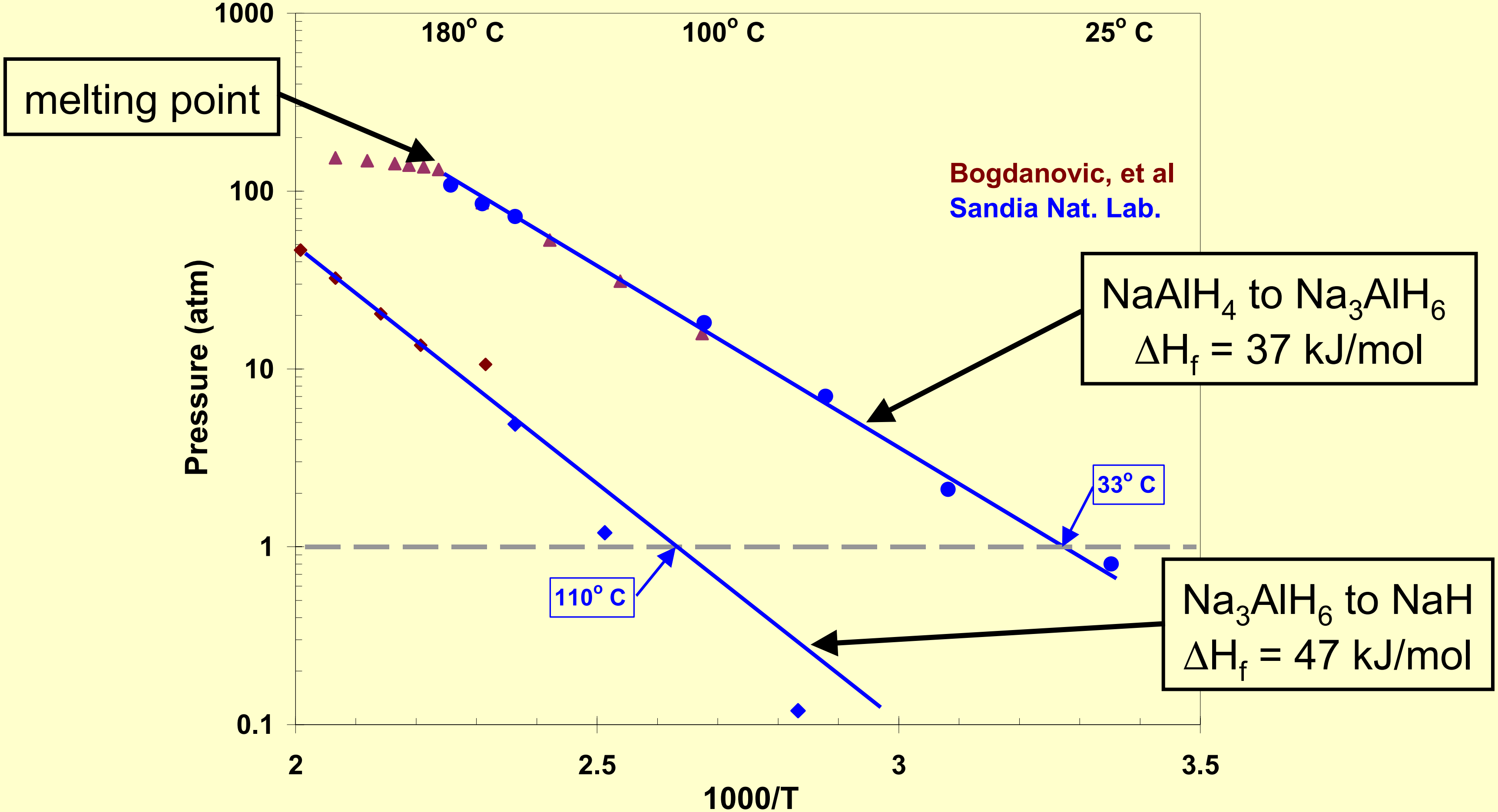
- There are five labs within USDOE program during FY02 working on complex-based hydrides, focused mainly on $NaAlH_4$
  - Univ. of Hawaii — Prof. C. Jensen
  - Sandia Nat. Lab. — Dr. K. Gross
  - Florida Solar Energy Center — Dr. D. Slattery
  - United Tech. Res. Center — Dr. D. Anton
  - Savannah River 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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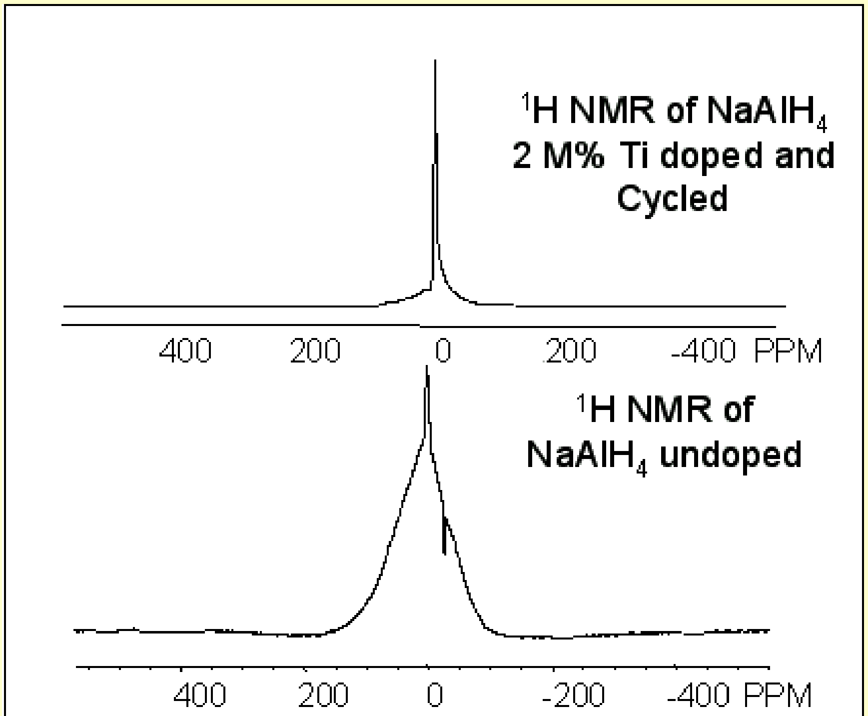
Current studies on $NaAlH_4$

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

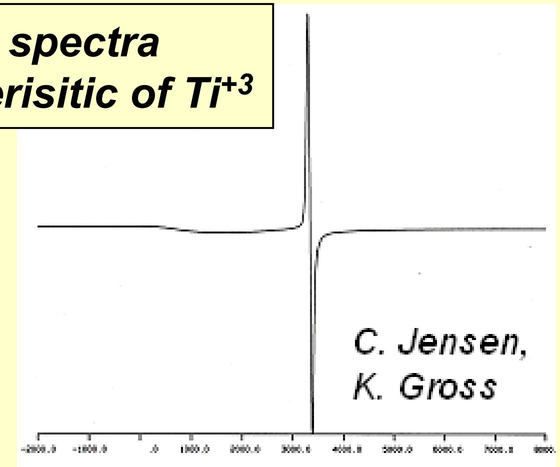
Understanding $NaAlH_4$ mechanisms will help in developing higher capacity hydrides

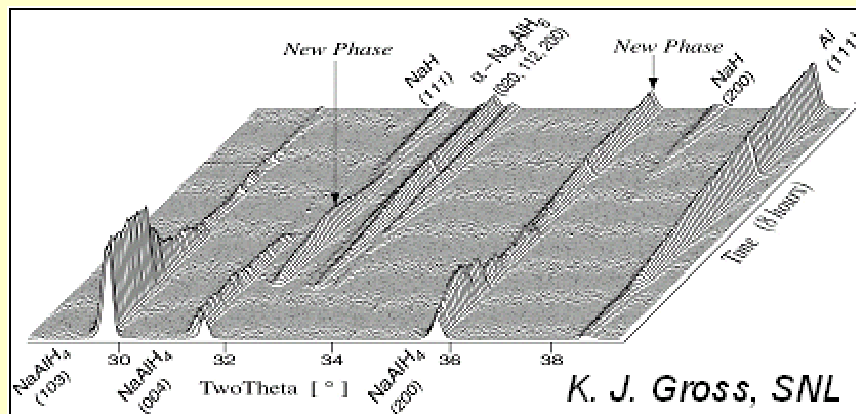
NMR shows Ti doping enhances proton mobility



C. Jensen, Univ. of Hawaii

ESR spectra characterisitic of Ti^{+3}





Decomposition of undoped $NaAlH_4$

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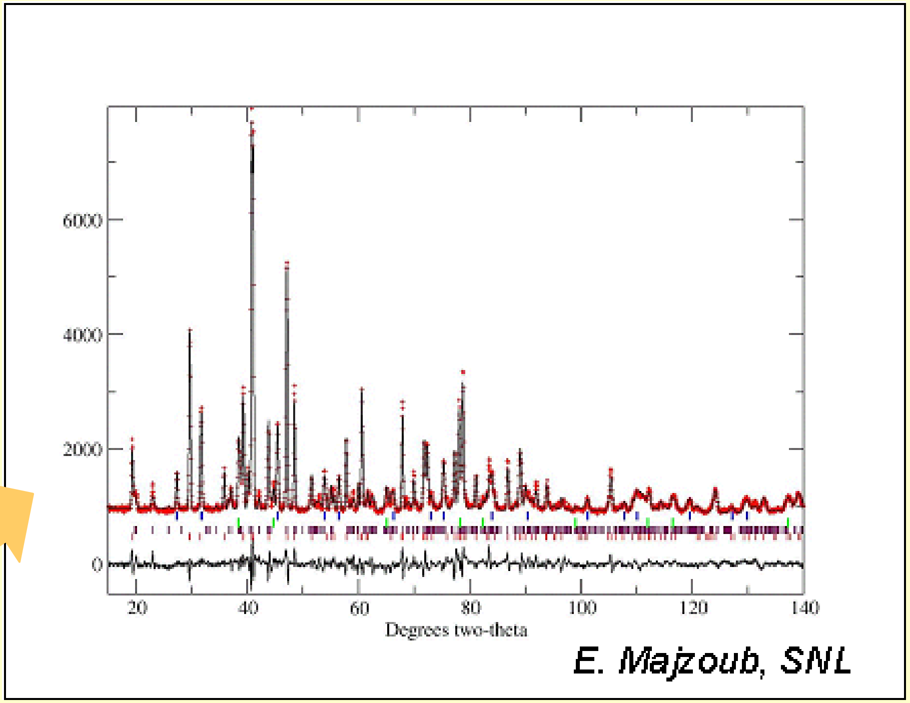
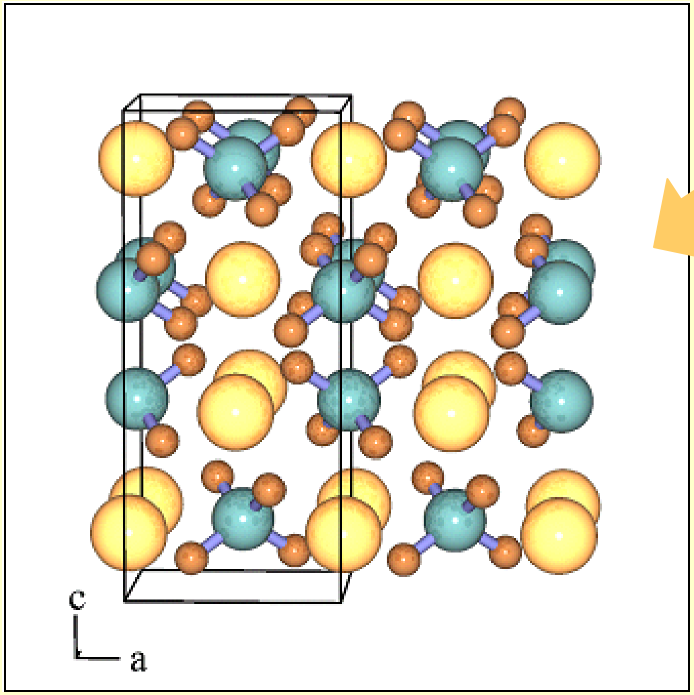
Crystal structure and modeling

Neutron diffraction
Rietveld refinement





***Ab initio* calculations using VASP**

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Catalysts/Doping

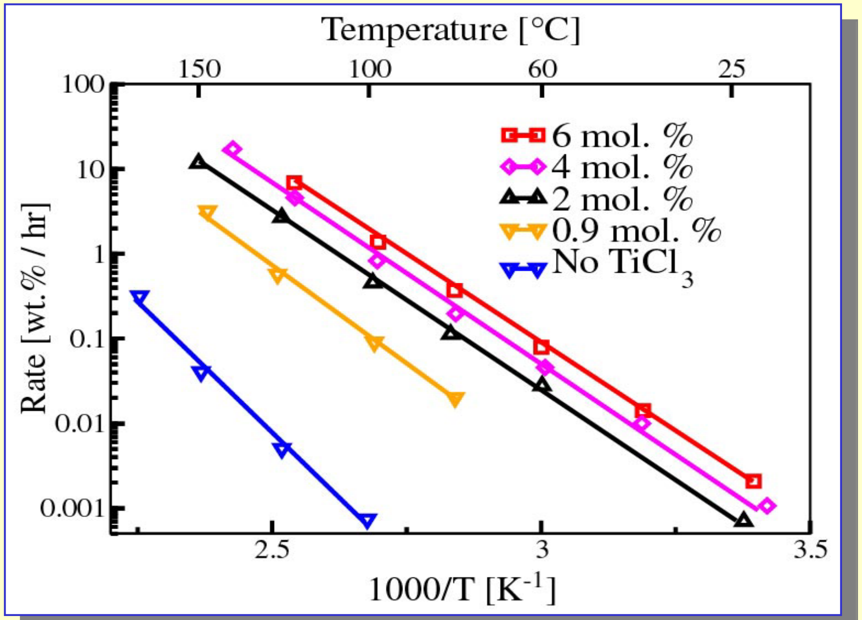
- Initially, reversibility believed due to catalytic effects.
  recent evidence, however, indicates bulk doping.
- 3 factors affect hydride performance:
  (1) catalyst/dopant
    - numerous compounds evaluated.
    - Ti-based most effective.

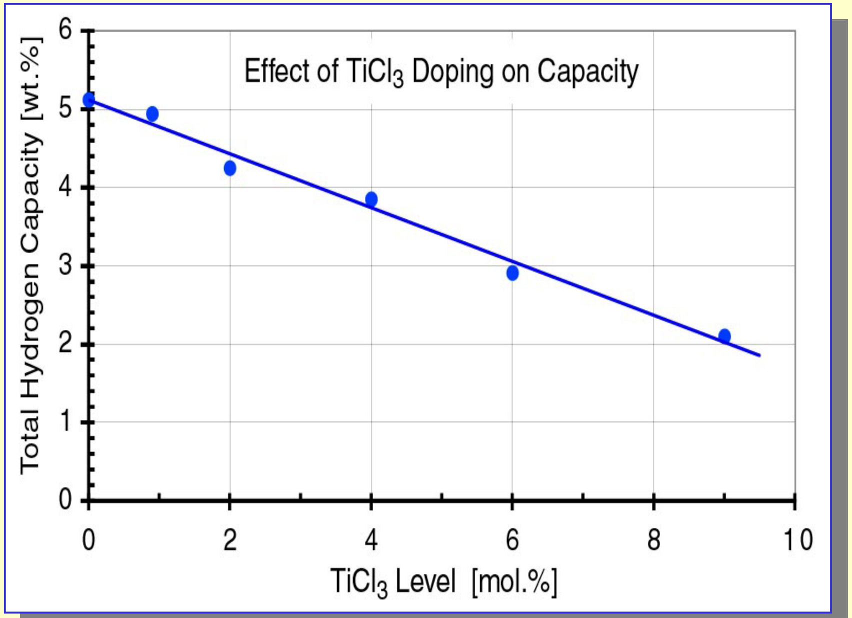
  (2) method of introduction
    - mechanical mixing (dry process)
    - wet chemistry
    - precursor must react with alanate

  (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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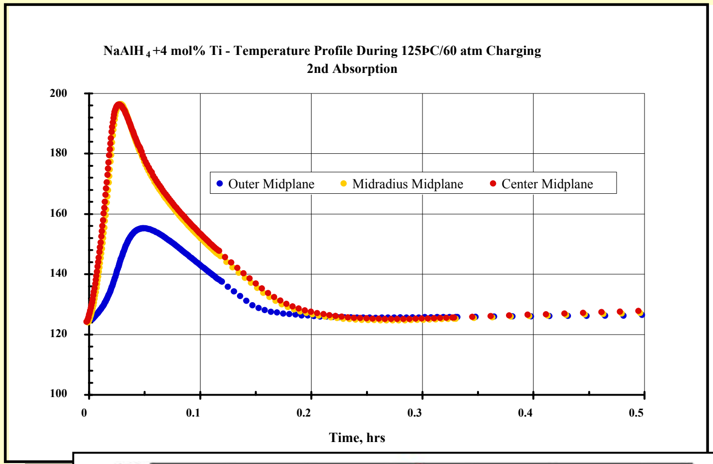
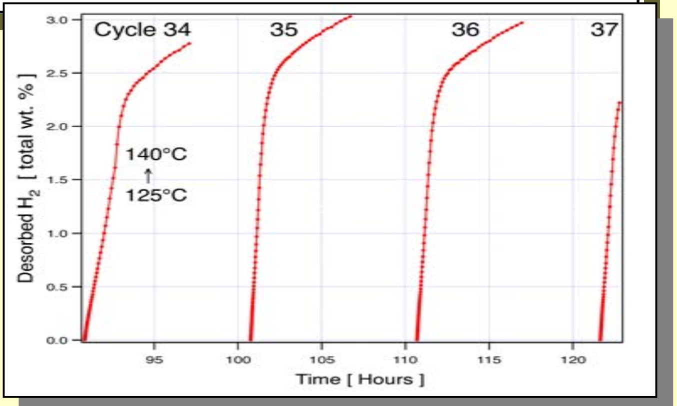
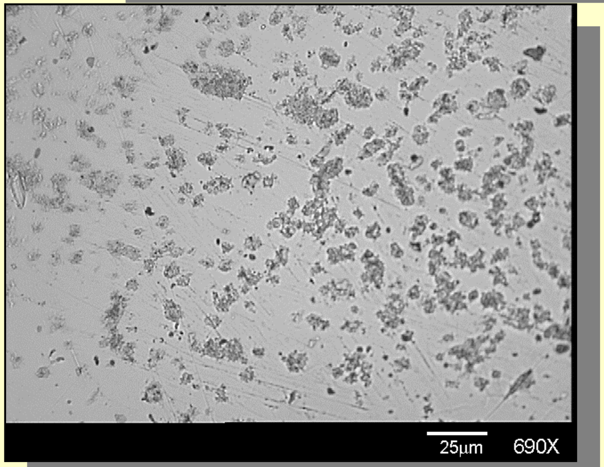
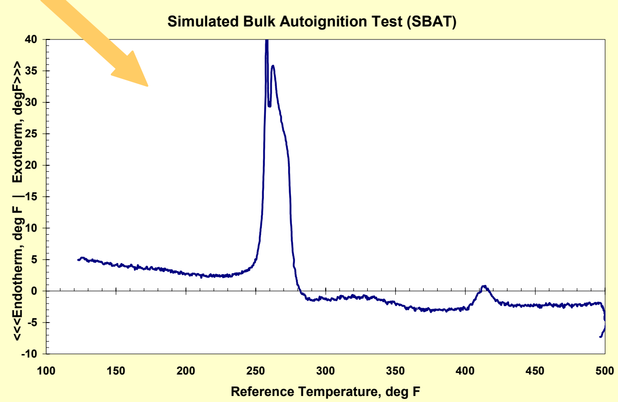
Engineering Properties

- 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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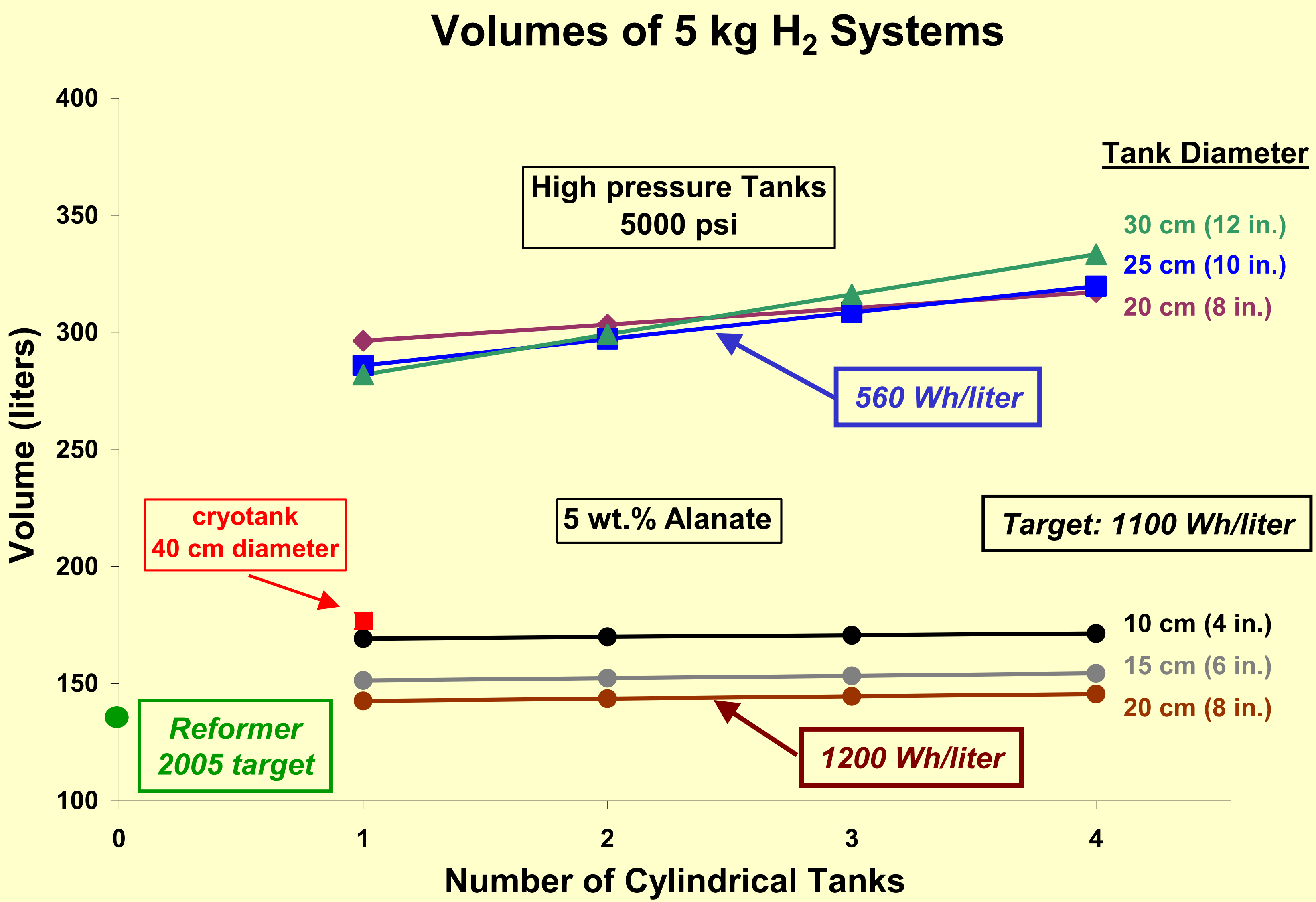
5 kg H_2 system volumes



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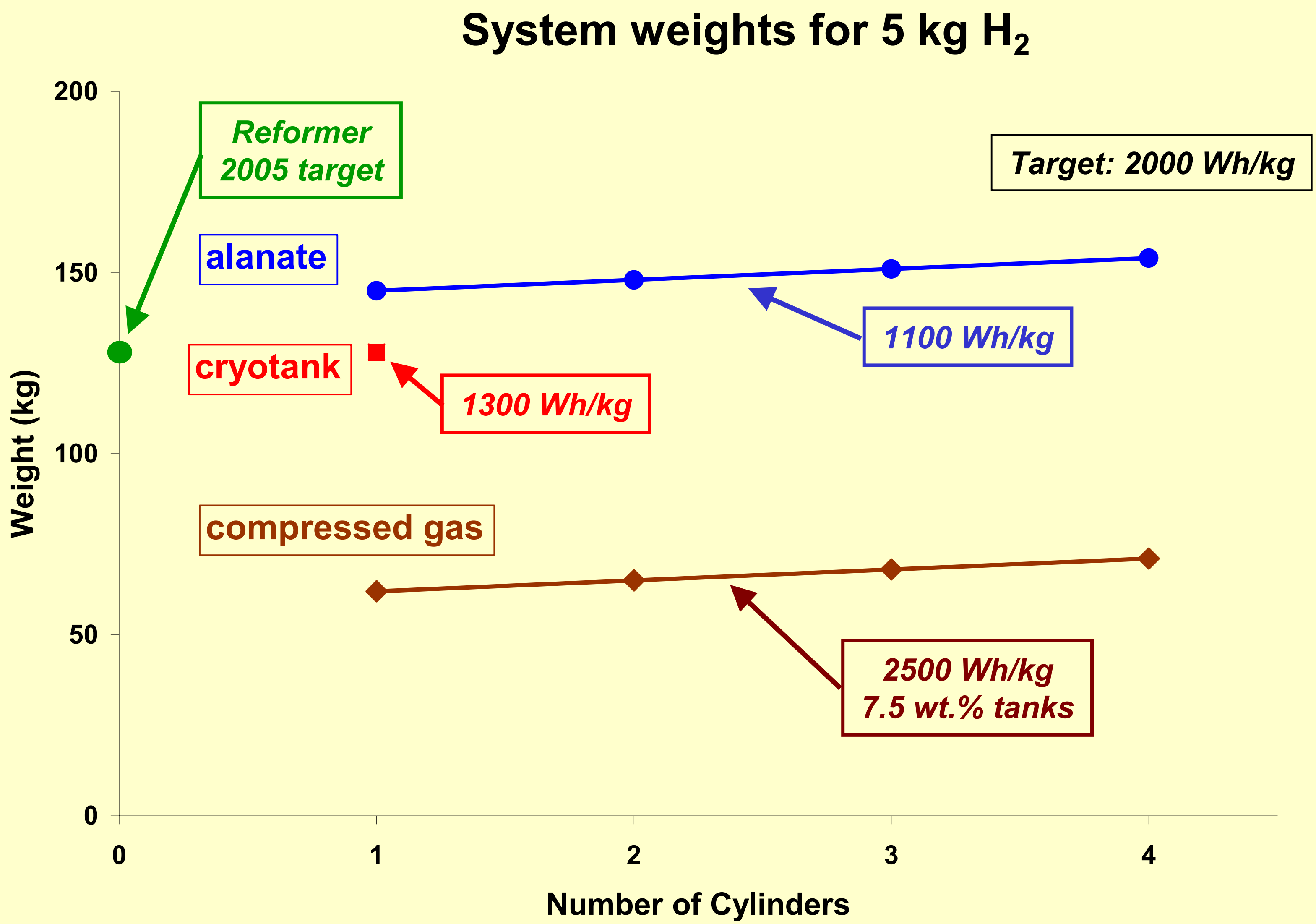
5 kg H_2 system weights



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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

$$\mathbf{NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 + heat}$$

**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!