Complex Hydrides for Hydrogen Storage

George Thomas, Consultant
Sandia National Laboratories
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?

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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?**

The online database [hydpark.ca.sandia.gov](http://hydpark.ca.sandia.gov) lists over 2000 elements, compounds and alloys that form hydrides.
**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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**Hydrogen can also form complexes with some elements**

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Complex hydrides give you another “knob to twist”

• Complex hydrides consist of a $\text{H}=\text{M}$ complex with additional bonding element(s)

• hydrogen complexes include:
  – $(\text{AlH}_4)^-$ (alanates)
  – $(\text{BH}_4)^-$
  – 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

- LiAlH$_4$
- NaAlH$_4$
- KAlH$_4$
- Be(AlH$_4$)$_2$
- Na$_2$LiAlH$_6$
- Mg(AlH$_4$)$_2$
- CuAlH$_4$
- Ca(AlH$_4$)$_2$
- Mn(AlH$_4$)$_2$
- Fe(AlH$_4$)$_2$
- AgAlH$_4$
- Ti(AlH$_4$)$_3$
- Ga(AlH$_4$)$_3$
- CsAlH$_4$
- Ti(AlH$_4$)$_4$
- In(AlH$_4$)$_3$
- Zr(AlH$_4$)$_4$
- Ce(AlH$_4$)$_3$
- Sn(AlH$_4$)$_4$

Increasing mol. weight

Weight percent hydrogen

0 2 4 6 8 10 12
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 coordinate 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**

\[ 3\text{NaAlH}_4 \overset{\text{catalyst}}{\leftrightarrow} \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \overset{\text{catalyst}}{\leftrightarrow} 3\text{NaH} + \text{Al} + 3/2\text{H}_2 \]

- **NaAlH\textsubscript{4}** to **Na\textsubscript{3}AlH\textsubscript{6}**
  \[ \Delta H_f = 37 \text{ kJ/mol} \]
- **Na\textsubscript{3}AlH\textsubscript{6}** to **NaH**
  \[ \Delta H_f = 47 \text{ kJ/mol} \]

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**Bogdanovic, et al**

**Sandia Nat. Lab.**

- melting point

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Current studies on NaAlH$_4$

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

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Understanding NaAlH$_4$ mechanisms will help in developing higher capacity hydrides.

NMR shows Ti doping enhances proton mobility.

ESR spectra characteristic of Ti$^{+3}$.

Decomposition of undoped NaAlH$_4$.

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C. Jensen, Univ. of Hawaii

K. J. Gross, SNL
Crystal structure and modeling

Neutron diffraction
Rietveld refinement

Ab initio calculations using VASP

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E. Majzoub, SNL
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

NaAlH₄

- Initial kinetics exhibit Arrhenius behavior
- Different activation energy in doped material
- Activation energy constant for 2 mol% and greater doping
- Faster kinetics with higher doping levels

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

- 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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Volumes of 5 kg H₂ Systems

- **High pressure Tanks 5000 psi**
  - 30 cm (12 in.)
  - 25 cm (10 in.)
  - 20 cm (8 in.)

- **5 wt.% Alanate**
  - cryotank 40 cm diameter
  - 560 Wh/liter

- **Target: 1100 Wh/liter**
  - 10 cm (4 in.)
  - 15 cm (6 in.)
  - 20 cm (8 in.)

- **Reformer 2005 target**
  - 1200 Wh/liter

- **5 kg H₂ system volumes**
  - 1200 Wh/liter
  - 560 Wh/liter
  - Target: 1100 Wh/liter
5 kg H₂ system weights

System weights for 5 kg H₂

- **alanate**: 1100 Wh/kg
- **cryotank**: 1300 Wh/kg
- **compressed gas**: 2500 Wh/kg

Target: 2000 Wh/kg

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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

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

- 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 NaAlH₄?
  – 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!

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