Hydrogen Storage
In Metal Hydrides

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Motivation

The Applications are here!
- Distributed Power Generation
- Portable Electronic Devices
- Fuel Cell Vehicles

But safe and practical Hydrogen Storage is not!

GM AUTOonomy

Secretarial Speeches

Remarks by Spencer Abraham on FreedomCAR
Detroit, MI
January 9, 2002

Welcome. Thank you all for coming. And I want to say how honored I am to be joined this morning by a very distinguished group of leaders. Sharing the podium with me today are Jack Smith, Chairman of General Motors’ Dieter Zetsche, President and CEO of the Chrysler Group and Will Boddie, Vice President of Global Core Engineering for Ford and Senator Carl Levin. I also want to recognize Representatives John Conyers, John Dingell, Joe Knollenberg, Sander Levin, and Lynn Rivers who are with us today. Thank you all for coming.

I also want to thank Governor John Engler for his energetic leadership and support of this important initiative for the auto industry. The Governor has a prior commitment in Lansing and is unable to attend today, but I want to acknowledge his assistance.

I am pleased to be here today to announce a new public-private partnership between my Department and the Nation’s automobile manufacturers to promote the use of hydrogen as a primary fuel for cars and trucks, and to reduce American dependence on foreign oil.
Objectives

- Practical hydrogen storage for hydrogen fuel cell vehicle
- Using reversible solid-state storage materials
- Demonstrate viability for vehicular and stationary applications

Goals

- Develop best materials for PEM fuel cell vehicle applications
- Expand knowledge of hydrogen sorption phenomena in solid-state media
- Improve performance: capacity, kinetics, thermodynamics, and cycle life
**Candidate Solid State Hydrogen Storage Media**

**Complex Aluminum Hydrides**

High Gravimetric Hydrogen Capacities!

<table>
<thead>
<tr>
<th>Example</th>
<th>Capacity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(AlH₄)</td>
<td>5.6 wt%</td>
</tr>
<tr>
<td>Li(AlH₄)</td>
<td>7.9 wt%</td>
</tr>
<tr>
<td>Zr(AlH₄)₂</td>
<td>3.9 wt%</td>
</tr>
<tr>
<td>Mg(AlH₄)₂</td>
<td>7.0 wt%</td>
</tr>
</tbody>
</table>

*Theoretical Reversible Capacities*
Background: Sodium Alanate - NaAlH₄

- Discovered: (Finholt & Schlesinger 1955)
- Direct Synthesis: THF, 140°C, 150 bar H₂ (Ashby 1958, Clasen 1961)
- Principal Use: Chemical Reducing Agent
- Characterization: (Dymova, Zakharkin, Claudy, Wiberg...)

- NaAlH₄ Melts 182°C
- PCT Desorption Measurements
- 2-step Decomposition

Reversible Hydriding of Sodium Alanates

Total Theoretical = 5.6 wt% hydrogen

\[ \text{NaAlH}_4 \rightleftharpoons \frac{1}{3}\text{Na}_3\text{AlH}_6 + \frac{2}{3}\text{Al} + \text{H}_2 \rightleftharpoons \text{NaH} + \text{Al} + \frac{3}{2}\text{H}_2 \]

3.7 wt% 1.9 wt%

Reversibility of sodium alanates under moderate conditions w/o solvents opened up a new class of Hydrogen Storage Materials!

( Bogdanovic' and Schwickardi, MH96 )

Bogdanovic, B. and M. Schwickardi
J. Alloys and Compounds, 253 (1997) 1

H₂ Re-absorption to form NaAlH₄
(Bogdanovic’ and Tölle)

- **Kinetic studies**
  - Wet doping (toluene, ether)
  - Ti/Fe - alkoxides catalysts
  - Ti/Fe/V/Zr/RE - chlorides

- **Thermodynamics**
  - PCT measurements

- **Mössbauer spec.**
  - Fe-Al compound

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**Recent developments in several groups**

- C.M. Jensen, University of Hawaii
- A. Zaluska & L. Zaluski, McGill University
- V.P. Balema, AMES Laboratory
- G. P. Meisner, GM R & D Center
- J. Chen, AIST

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Sandia National Laboratories
Research and Development of Sodium Alanates

Total Theoretical Capacity = 5.6 wt% hydrogen

\[ \text{NaAlH}_4 \Rightarrow \frac{1}{3}\text{Na}_3\text{AlH}_6 + \frac{2}{3}\text{Al} + \text{H}_2 \Rightarrow \text{NaH} + \text{Al} + \frac{3}{2}\text{H}_2 \]

3.7 wt.%

1.9 wt.%
Understanding Hydrogen Sorption Process

A) NaAlH_4: foundation for complex hydride development

- Developed Dry Doping using solid TiCl_3

B) Extend knowledge gained to other complex hydrides
Phase Transitions & Reaction Rates

Decomposition of undoped NaAlH₄ on heating to 175°C

- Anisotropic lattice expansion on heating
- Observed formation of metastable intermediate phase
- Determined rates of individual reactions
Different Rates: Two or Three Step Decomposition Reaction?

\[ \text{NaAlH}_4 + 2\text{NaH} \Rightarrow \text{Na}_3\text{AlH}_6 \]

- Thermal desorption: NaAlH\textsubscript{4} + 2NaH doped with TiCl\textsubscript{3}
- No evidence for back reaction
Continuing Crystal Structure Studies

- Neutron Scattering NaAlH4 performed (collaboration with NIST)
- Neutron Diffraction NaAlD4 completed (collaboration with NIST)
- New in-house in-situ XRD capabilities installed

Inel 120º PSD + Rotating Anode: Full Scans < 1 minute
Thermodynamics

\[ \Delta H (\text{NaAlH}_4) = -37 \text{ kJ/mol H}_2 \]

\[ \Delta H (\text{Na}_3\text{AlH}_6) = -47 \text{ kJ/mol H}_2 \]
Comparison with other Hydrides

van’t Hoff Diagram

- NaAlH₄ is a low temperature hydride
- Na₃AlH₆ is one of the few medium temperature hydrides
New Methods of Synthesis - Improved Doping Process

- **Generation I:**
  Ti/Zr-Alkoxide liquid Catalyst
  NaAlH₄ dried from THF

- **Generation II:**
  TiCl₃ solid Catalyst
  NaAlH₄ dried from THF

- **Generation IIIa:**
  Direct Synthesis and Doping:
  NaAlH₄ is formed Directly from NaH and Al. Purification in THF solvent no longer required!

- **Generation IIIb:**
  Direct Synthesis and Doping:
  NaAlH₄ from Na and Al. Reduces raw material cost!
  (patent application submitted)

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RGA Impurities in Desorbed Hydrogen

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Analytical Materials Science Dept.
Effect of Catalyst Loading on Capacity

- Reversible Hydrogen Capacity decreases with TiCl₃ doping level

- XRD showed the formation of NaCl through the reaction:

  \[ 3\text{NaAlH}_4 + \text{TiCl}_3 \rightarrow \text{Ti} + 3\text{NaCl} + 3\text{Al} + 6\text{H}_2 \]
**Arrhenius Kinetics Measurements**

Isothermal Desorption Rates v.s. Temperature

**NaAlH$_4$**

**Na$_3$AlH$_6$**

Effect of Catalyst Loading on Reaction Rates

NaAlH$_4$ doped with 0–6 mol.% TiCl$_3$

Rate = $k \exp(-Q/RT)$

- Activation Energy changes with introduction of Ti - Different Mechanism
- Activation Energy is independent of catalyst doping level
- Contrary to generally held view: Rates increase with catalyst content
Trade-off between Capacity & Kinetics

- Reversible Hydrogen Capacity decreases with TiCl₃ doping level
- Desorption (and Absorption) Kinetics increases with TiCl₃ doping level
- There is a trade-off between improved kinetics and capacity loss
Doping With Other Titanium-Halides

NaAlH₄ Isothermal Desorption Rates v.s. Temperature

- Activation Energies are identical for TiCl₃ and TiF₃
- Only Ti responsible for enhanced kinetics and reversibility
Cycle-Life Studies

NaAlH$_4$ doped with 4 mol.% TiCl$_3$

- Activation effect enhances kinetics in first Cycles
- Little change after initial cycles!
**Generation III-D Alanates: Indirect Doping Process**

- **TiCl₂ Pre-reacted with LiH**
- **Requires initial activation cycles**
- **Suggests solid-state diffusion and substitution**
Evaluation of Engineering Properties of Complex Hydrides

- Scaled up test bed studies
  (in-house studies in collaboration with Gary Sandrock and George Thomas)

Scaled up engineering test bed

![Graph showing temperature profile during charging](chart.png)
Studies of Material Safety Issues

Interaction of Alanates with Containment Vessel Materials

- Leaching observed in Aluminum materials due to 50% aluminum deficient composition
- Lead to Long-term cycling studies of interaction between Alanates and vessel materials

Optical micrographs 6061 Al coupon

Automated hydrogen cycling apparatus
Conclusion

- 1 atm $H_2$ released at: $NaAlH_4$ (33 °C ) and $Na_3AlH_6$ (110 °C )

- Reversible capacity above 4 wt.%

- Trade-off between improved kinetics and in capacity

- Sorption properties independent of Ti-halide precursor

- Direct Synthesis: Enhanced kinetics, no gaseous contaminants, reduced cost and complexity

- Some safety aspects of containment materials tested
Outlook

To meet the requirements of fuel cell applications:

- Kinetics must be improved
  - Advanced catalysts and doping procedures

- Second reaction plateau pressure must be increased
  - Elemental substitution

- Long-term cycling must be demonstrated
  - Further investigations into capacity loss

- Safety issues must be evaluated and addressed
  - Engineering design and materials modification

- A better understanding of the reaction mechanisms is needed
  - Fundamental studies will aid the development of advanced materials
Special Acknowledgement

Steve Goods - Hydrogen Materials interaction
Eric Majzoub - Hydrogen Storage Materials
Don Meeker - Hydride Chemistry
Andreas Orozco - Summer Student
Brian Somerday - Hydrogen Materials interaction
Gary Sandrock - Hydrogen Storage Materials
Scott Spangler - XRD
George Thomas - Hydrogen Storage Materials
Nancy Yang - Microscopy

Thank you!
Progress in Reversible $H_2$ Storage Capacity

(Inexpensive Room Temperature Hydrides)