Chemical Storage - Overview

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Hydrogen Fuel - Attributes

- $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ (1.23 V)
- High gravimetric energy density: 27.1 Ah/g, based on LHV of 119.93 kJ/g
- 1 wt % = 189.6 Wh/kg (0.7 V; *i.e.* η_{FC} = 57%)
- Li ion cells: 130-150 Wh/kg

Chemical Hydrides - Definition

- They are considered secondary storage methods in which the storage medium is expended – primary storage methods include reversible systems (e.g. MHs & C-nanostructures), GH_2 & LH_2 storage

Chemical Hydrides – Definition (cont.)

- The usual chemical hydride system is reaction of a reactant containing H in the “-1” oxidation state (hydride) with a reactant containing H in the “+1” oxidation state

Chemical Hydrides – Definition (cont.)

- Include simple ionic hydrides having hydride ion H-, which is a very strong reducing agent
- Complex hydrides have the general formula $M(M'H_4)_n$, where n is the valance of M, and M' is a trivalent Group 13 element

Chemical Hydrides – Definition (cont.)

- Reactions include chemical hydride (e.g. LiH, NaH, AlH_3, $LiAlH_4$, Li_3AlH_6, $NaBH_4$, etc.) & a proton containing reactant (e.g. H_2O, NH_3 & H_2S)

Chemical Hydrides – Requirements

- Be thermodynamically spontaneous ($\Delta G<1$)
- Be kinetically tractable (fast, but not explosive)
- Use available (cheap, etc.) reactants

Chemical Hydrides – Requirements (cont.)

- Produce H_2 compatible with the PEM fuel cell (no H_2S, CO or NH_3)
- Can provide H_2 to the fuel cell as the H_2 is needed (load following) without complex & heavy control systems

Chemical Hydrides – H_2 Generation

- Hydrolysis
  - – reaction with H_2O, NH_3, H_2S, etc.
- Pyrolysis
  - – decomposition by heat

Chemical Hydrides – H_2 Generation by Hydrolysis

Reaction	wt% H_2 Yield	Capacity, kWh/kg
$LiH + H_2O \rightarrow LiOH + H_2$	7.7	1.46
$NaH + H_2O \rightarrow NaOH + H_2$	4.8	0.91
$CaH_2 + 2 H_2O \rightarrow Ca(OH)_2 + 2 H_2$	5.2	0.99
$LiAlH_4 + 4 H_2O \rightarrow LiOH + Al(OH)_3 + 4 H_2$	7.3	1.38
$LiBH_4 + 4 H_2O \rightarrow LiOH + H_3BO_3 + 4 H_2$	8.6	1.63
$NaAlH_4 + 4 H_2O \rightarrow NaOH + Al(OH)_3 + 4 H_2$	6.4	1.21
$NaBH_4 + 4 H_2O \rightarrow NaOH + H_3BO_3 + 4 H_2$	7.3	1.38

Chemical Hydrides – H_2 Generation by Hydrolysis (cont.)

- Kinetics are inhibited by high pH & insolubility of reaction products
  - use of catalyst: Ru supported on ion exchange resin (Millennium Cell)
  - use of steam (Matthews, et al.)
  - hydride slurry (Thermo Power)

Chemical Hydrides – H_2 Generation by Hydrolysis (cont.)

- Reactions are spontaneous & highly exothermic
  - use of ligand-stabilized complexes (Matthews, et al., IJHE 23(12) 1998)
- Reactions are irreversible & by-products needs recycling or disposal

Chemical Hydrides – H_2 Generation by Hydrolysis (cont.)

- H_2 can be produced from stoichiometric reaction but, in practice,excess water is almost always required
- Most are moderately to very unstable when stored in humid air

Chemical Hydrides – H_2 Generation by Hydrolysis (cont.)

- More difficult issue is the control of the reaction & choosing the lightest possible system
- To be able to compete with primary Li batteries on cost, than the reactants must be cheap and the generation must be simple

Chemical Hydrides – H_2 Generation by Hydrolysis (cont.)

- The inorganic hydrides that are used industrially (e.g. $LiAlH_4$) & common reactants (*i.e.* H_2O or NH_3) have the best chance to meet cost goals

Chemical Hydrides – H_2 Generation by Hydrolysis (cont.)

- $LiAlH_4 + 2NH_3 \rightarrow LiNH_2 + AlN + 4H_2$
  (\$50/lb)+(\$1/lb)
- gives a cost of reactants of about \$0.024/Wh & energy density of about 2514 Wh/kg

Chemical Hydrides – H_2 Generation by Pyrolysis

- One application Combines primary hydrides with NH_4Cl or similar halide salt, stabilized with a polymer binder (e.g. PTFE):
  $NH_4F + LiBH_4 = LiF + BN + 4\ H_2$
  - H_2 storage density of ~ 13.6 wt %

Chemical Hydrides – H_2 Generation by Pyrolysis (cont.)

- NH_4X + MH formulations render compound storable, and insensitive to air & moisture
- But - these pyrolytic reactions are highly exothermic & can NOT be stopped once initiated

Chemical Hydrides – H_2 Generation by Pyrolysis (cont.)

- NH_4BH_4 = BN + 4 H_2 (24.5 wt %) Unstable above -20°C, unsuitable
- NH_3BH_3 = BN + 3 H_2 (20 wt %) Requires heating, decomposition at stages from ~130-450°C

Chemical Hydrides – H_2 Generation by Pyrolysis (cont.)

- Artz & Grant (US 4,673,528)
  - – $Mg(BH_4)_2.2NH_3/LiNO_3/PTFE$: 85/7½/7½ wt %
  - – gives 12.84 wt% of 99.8% pure H_2
  - – impurities include CO, NH_3 & CH_4
  - – once reaction starts, can NOT be stopped

Chemical Hydrides – H_2 Generation by Pyrolysis (cont.)

- Artz & Grant (US 4,468,263)
  - $NH_3BH_3/N_2H_4.2BH_3/(NH_4)_2B_{10}H_{10}/NH_4NO_3$: 50/30/9.8/10.2 wt %
  - gives 16.52 wt% of >94% pure H_2
  - impurities include borazine $B_3N_3H_6$
  - reaction unstoppable once started
  - DDT occurs in some cases

Chemical Hydrides – Cost/Performance Comparison

Hydrogen storer	Mass, kg	Volume, l	Cost, US$	Reference
LiH	1.7	3.7	109	1
CaH_2	4.5	4.0	104	1
$NaBH_4$ (35 wt% aqueous)	6.21	6.21	102	1 & 2
H_3BNH_3	2.38	3.21	390-525	-

1. V.C.Y. Kong, et al., Int. J. Hydrogen Energy, 24, 665-75, 1999
2. S.C. Amendola, et al., Proceedings of the Power Sources Conference, 39th, 176-79, 2000

Conclusions

- Successful implementation of chemical hydrides for vehicular FC applications requires:
  - Substantial reduction in their production costs
  - Development of new synthesis routes for their preparation