Structures and effect of additives in alanates

Institute for Energy Technology

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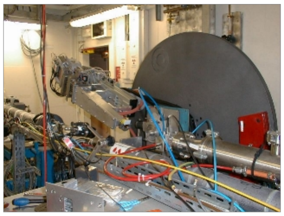
Introduction

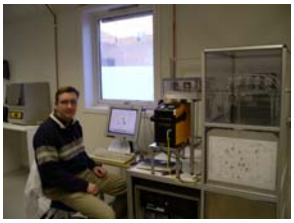
Alanates – metal hydrides based on the AlH_4^- or the AlH_6^{3-} units - are one of the most promising groups of metal hydrides for reversible hydrogen storage at moderate temperatures. Additives are important for dehydrogenation and hydrogenation. This was discovered by Bogdanovic et al in 1997 for $NaAlH_4$ with Ti additives. In order to improve the kinetics, a better understanding of the additives through detailed studies of structural and thermodynamic properties is essential.

Experimental



X-ray diffraction

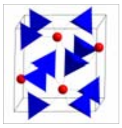
Neutron diffraction



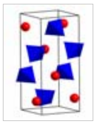
PC isotherms

Results

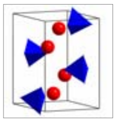
Crystal structure determination



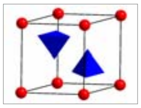
$LiAlD_4$



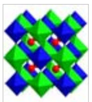
$NaAlD_4$



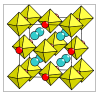
$KAlD_4$



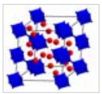
$Mg(AlH_4)_2$



Na_2LiAlD_6



K_2NaAlH_6

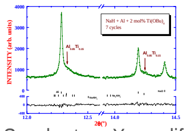


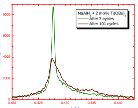
Li_3AlD_6

Ti additives in alanates

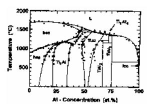
- No difference of unit-cell dimensions from pure alanate
  - No solid solution in crystalline bulk
- No crystalline Ti-compounds. Even for 10% $TiF_3/TiCl_3$
  - Amorphous Ti compound? (Ti-rich Ti-Al?)

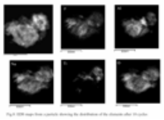
- Shoulder at Al observed after cycling
  - For $Ti(OBu)_4$, $TiCl_3$ and TiF_3
  - Increasing intensities with increasing Ti content
  - $Al_{1-y}Ti_y$, $y = 0.15$





Synchrotron X-ray diffraction: 7& 101 cycles

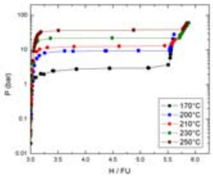


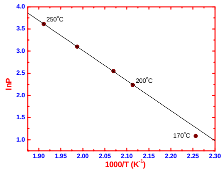


Ti-Al Phase diagram TEM

Mixed alanates

K_2NaAlH_6 and K_2LiAlH_6 predicted to be stable – in addition to Na_2LiAlH_6.

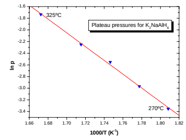




Isotherms Na_2LiAlH_6
$\Delta H = 56.4$ kJ/mol, $\Delta S = 137.9$ J/K mol H_2

New alanate found: K_2NaAlH_6

Mixed alanates more stable than monoalkali-alanates.



Takes ordered perovskite structure: $A_2BB'H_6$
A large, B smaller, B' = Al
Similar to Na_3AlH_6 [$=Na_2(NaAl)H_6$]
which have rotated octahedra
At higher temperature Na_3AlH_6 is cubic
due to disappearance of rotation.

Conclusions

Structural investigations have determined the crystal structure of a number of alanates

Partial results on the Ti additives in alanates: After cycling, around 80% of it is bound as $Al_{1-y}Ti_y$, $y \approx 0.15$

Stability of mixed alanates found to be higher than monoalkali-alanates

New alanate synthesized: K_2NaAlH_6