Supporting Information

Ionic liquids as an efficient media assisted mechanochemical synthesis of α-AlH_3 nano-composite

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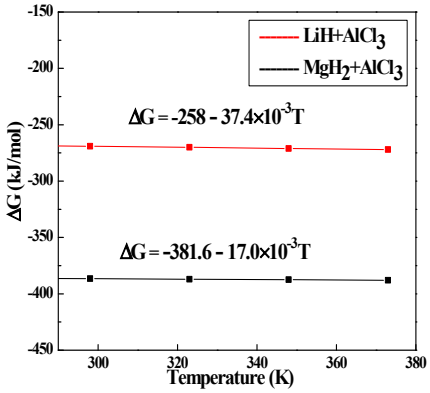

Fig. S1 Free energy of reaction between MgH_2-$AlCl_3$ and LiH-$AlCl_3$ at a temperature range of 273-373K

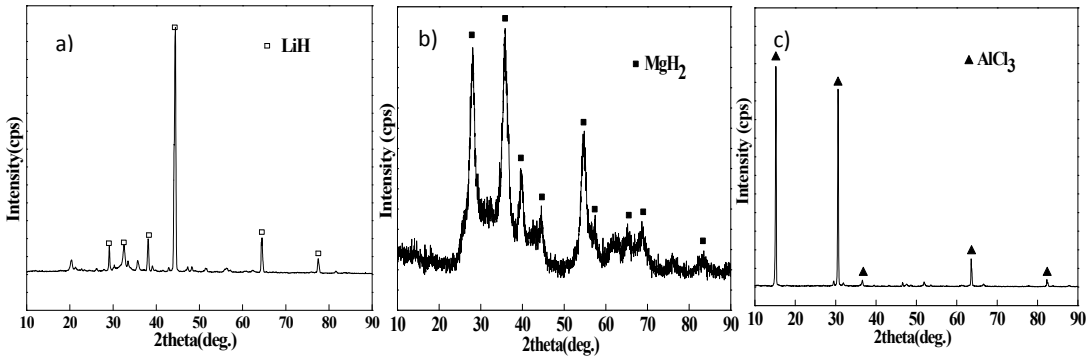

Fig. S2 XRD patterns of a) LiH phase, b) Mg powders milled in hydrogen for 20h, c) $AlCl_3$ phase

It is suggested from Fig. S2b) that the MgH_2 phase was fully formed until milling Mg in hydrogen for 20 h. Calculated by Scherrer equation based on the XRD patterns, the average crystallite size of MgH_2 can reach 10 nm. For nanostructured MgH_2 prepared by ball milling, the activation energy for dehydrogenation can be reduced significantly because there are much more grain boundaries and crystal defects which result in the raising of the average atomic energy level. For example, it was reported by Ouyang[1, 2] that Mg(In) solid solution provides a new way to tune the dehydriding thermodynamics of MgH_2. But, the activation energy for thermally driven dehydriding of MgH_2 was still to be 127.7 kJ/mol. In the present study, the activation energy of prepared MgH_2 is found to be 82.7 kJ/mol, which is much lower than that reported in Ref. 1 and 2. Thus, nanocrystalline MgH_2 powders prepared by mechanochemical reaction has an excellent reactivity.

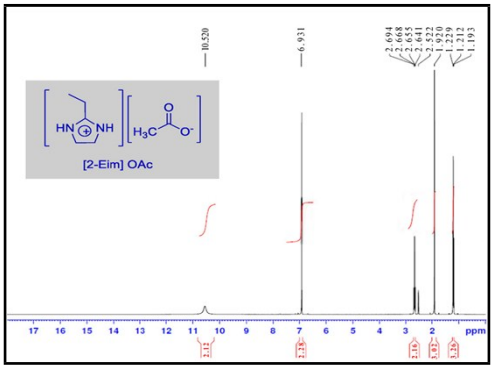

Fig. S3 ^{1}H NMR of 2-ethyl imidazolium acetate [2-Eim] OAc

^{1}HNMR spectra of the [2-Eim]OAc ionic liquid is shown in Fig. S3. The important spectral data of [2-Eim] OAc were presented: δ (ppm) 10.52 (s, 2H, N-H), 6.93 (s, 2H), 2.6 (m, 2H. CH_2), 1.92 (s,CH_3), 1.20 (t, 3H, CH_3). It is noted that the important peak of [2-Eim] OAc is related to the hydrogens (N–H) which observed in 10.52 ppm.

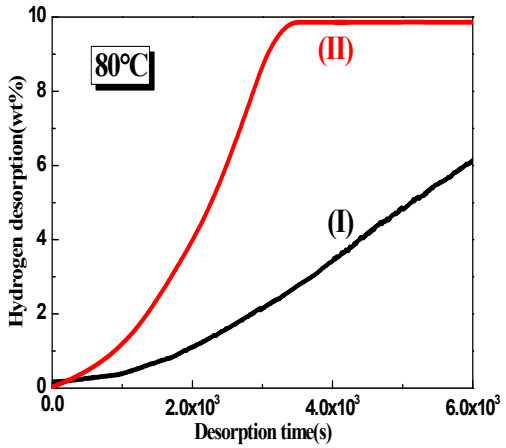

Fig. S4 The de-hydriding curves of α-AlH_3 nanocomposite heated at 80°C: (I) α-AlH_3/LiCl nanocomposite (II) α-AlH_3/LiCl doped with LiH.

It was demonstrated by Sandrock[3] that the onset decomposition temperature of AlH_3 can be reduced to below 100°C by LiH addition. According to Sandrock's report, 2mol% LiH was added into α-AlH_3/LiCl nano-composite. It can be seen from Fig.S4 that when the dehydriding temperature was fixed at 80°C, the time of full decomposition decreased rapidly. Compared with the α-AlH_3/LiCl nano-composite without adding LiH, AlH_3 added with LiH has a perfect dehydriding property with a 9.86wt.% of hydrogen content at 80°C for 3400 s. This results have good correspondence with the report addressed by Sandrock who also found that decomposition kinetics of AlH_3 can be accelerated with the effect of the LiH doping.[3]

Reference

[1] L. Z. Ouyang, Z. J. Cao and H. Wang, Enhanced dehydriding thermodynamics and kinetics in Mg(In)-MgF_2 composite directly synthesized by plasma milling. *J. Alloy. Compd.*, 2014, **586**, 113-117.

[2] L. Z. Ouyang, X. S. Yang and H. W. Dong, Structure and hydrogen storage properties of Mg_3Pr and $Mg_3PrNi_{0.1}$ alloys. *Scripta Mater.*, 2009, **61**, 339-342.

[3] G. Sandrock, J. Reilly, J. Graetz, w.-m. Zhou, J. Johnson and J. Wegrzyn, Accelerated thermal decomposition of AlH_3 for hydrogen-fueled vehicles. *Appl. Phys. A*, 2005, **80**, 687-690.