Supplementary Information

Enhanced hydrogen sorption in Li-Mg-N-H system by synergistic role of $Li_4(NH_2)_3BH_4$ and $ZrFe_2$

Vivek Shukla [a], Ashish Bhatnagar [a], Pawan Soni [a], Alok K.Vishwakarma[a], M A Shaz [a], T P Yadav [a], O N Srivastava [a*]
[a]*Hydrogen Energy Centre, Department of Physics, Banaras Hindu University, Varanasi-221005, India*

Corresponding author: email: heponsphy@gmail.com

S1

During the dehydrogenation of TT L-M and TT L-M-B-Z sample, the gaseous products were analyzed by Gas Chromatography (GC) using two types of columns i.e. Carbosphere and Chromosorb Columns (Fig-S4 (i-iv)). In the Carbosphere column, only H_2 and N_2 can be detected, however in Chromosorb column both H_2 and NH_3 can be detected. It has been found from GC measurement that TT L-M contains, H_2 and NH_3 whereas TT L-M-B-Z sample contains 99.90 % of H_2 were detected and the peak that of NH_3 is not discernible. These results suggest that $LiBH_4$ added sample suppresses the NH_3 liberation during dehydrogenation.

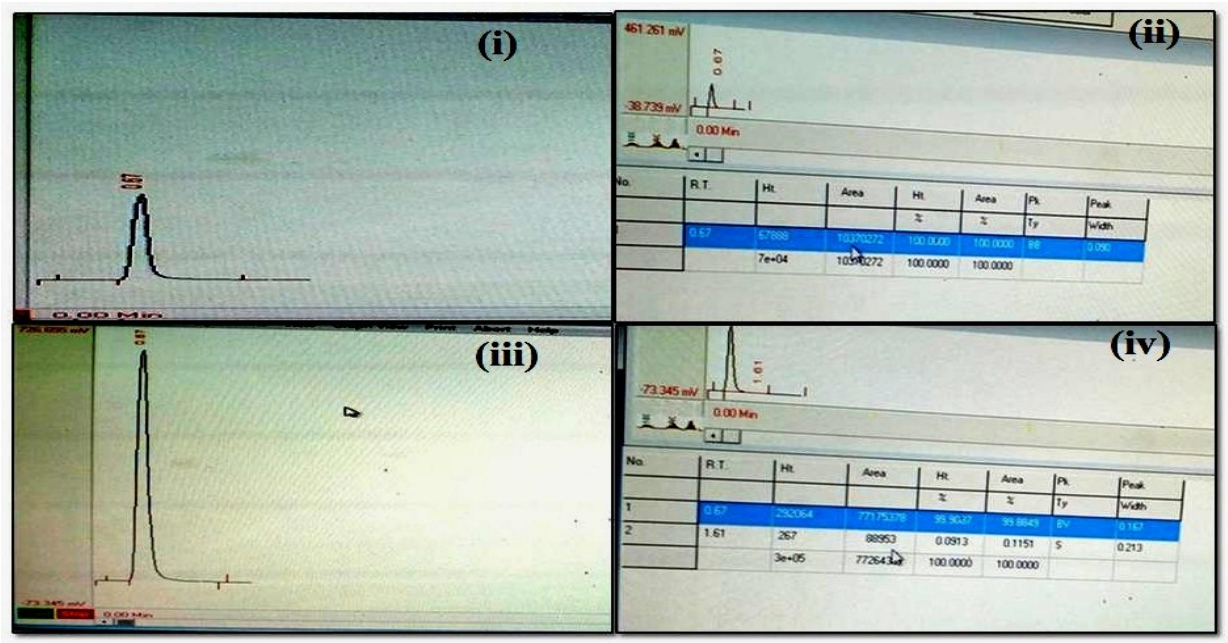

Figure. S1 Gas chromatography (GC) measument using Carbosphere and Chromoasorb coluomns (i-ii) Detection of pure H_2 in Chromosorb coloumn (iii-iv) Detection of evovled gases on the dehydrogenation of TT L-M-B-Z sample in Chromosorb coloumn.

S2

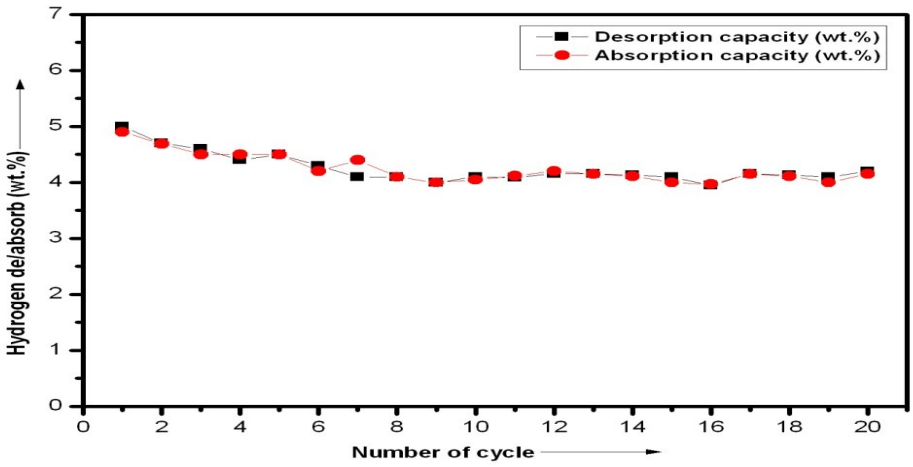

Figure. S2 Storage capacity upon cycling (180^{o}C and 7 MPa) of catalysed TT L-M-B-Z composite.

S.3

Synthesis of $Li_4(NH_2)_3BH_4$ and it's effect on hydrogen sorption in 2 $LiNH_2$-1.1MgH_2-0.1$Li_4(NH_2)_3BH_4$

The synthesis of $Li_4(NH_2)_3BH_4$ has been done by ball milling of $LiNH_2$ and $LiBH_4$ in ratio of 3:1 for 20 hours at 200 rpm under 1MPa H_2 pressure. The ball milled material have been characterized by XRD, which shows that the synthesized material is $Li_4(NH_2)_3BH_4$. Afterwards the as synthesized material ($Li_4(NH_2)_3BH_4$) was mixed with $LiNH_2$-MgH_2. The molar ratio of $LiNH_2$:MgH_2: $Li_4(NH_2)_3BH_4$ (L-M-Q) was taken to be 2:1:0.1 . Ball milling of L-M-Q was done for 10hrs at 200 rpm under 1 MPa of H_2 pressure. Fig.S2(i-a) depicts the XRD of ball milled LMQ which shows dominant presence of $LiNH_2$ and MgH_2 with some weak peaks of $Mg(NH_2)_2$ .After thermal treatment (200°C and 7MPa H_2 pressure) of L-M-Q sample (TT L-M-Q), it was observed that (Fig. S2(i-b)) peaks of $LiNH_2$ and MgH_2 were present together with some less intense peaks of $Mg(NH_2)_2$/LiH, which indicates that $LiNH_2$ and MgH_2 remains mainly unreacted even after annealing. On the other hand, in case of in-situ formed quartenary hydride catalyzed Li-Mg-NH system (TT-L-M-B), there is almost complete formation of $Mg(NH_2)_2$/LiH (phase having reversible H_2 storage) even after ball milling. Fig.S2(ii) displays the TPD curve of TT L-M-Q composite where the onset desorption temperature is ~200°C with total release of 5.50wt.% H_2 up to 350°C. However in case of TT-L-M-B the onset desorption temperature is 150°C with a total release of 5.20 wt.% H_2 up to 300°C.

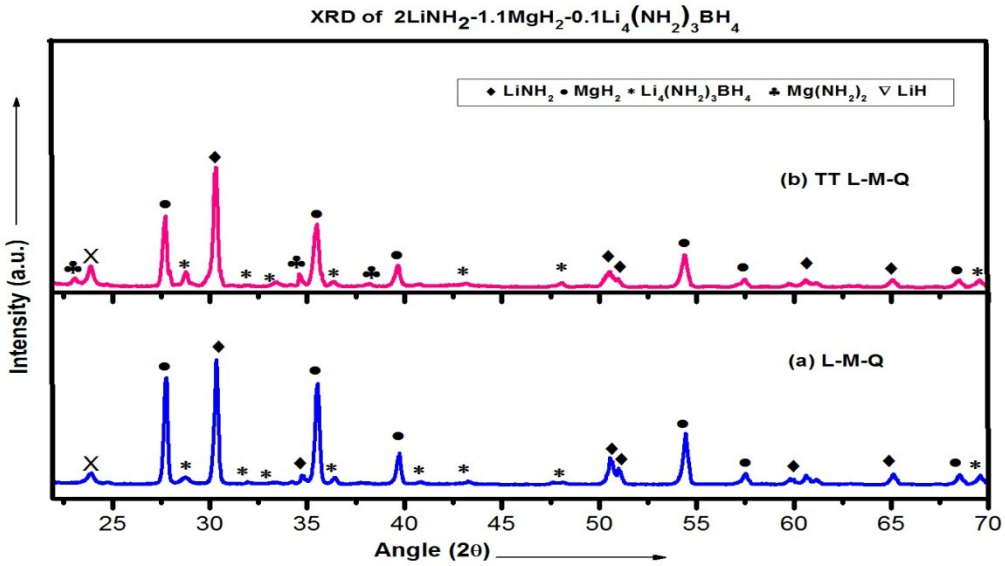

Fig.S2(i) XRD of L-M-Q and TT L-M-Q sample

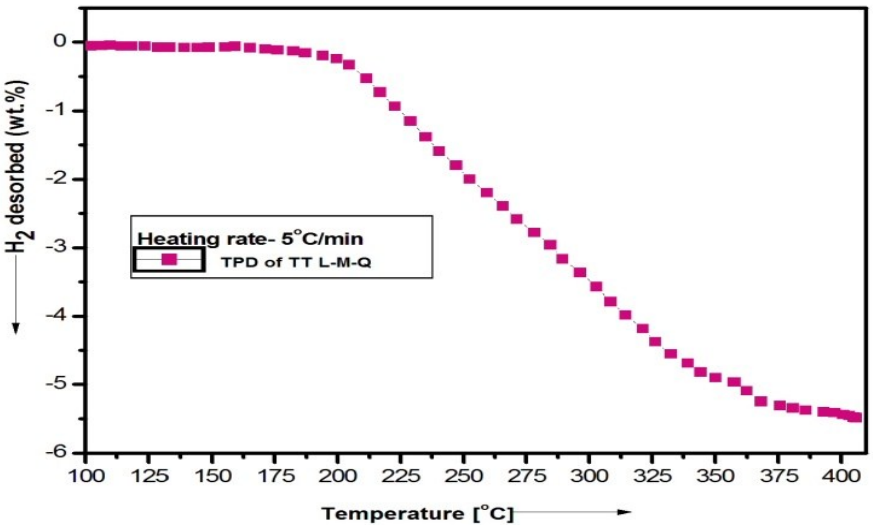

Fig.S2(ii) TPD of TT L-M-Q sample

S4

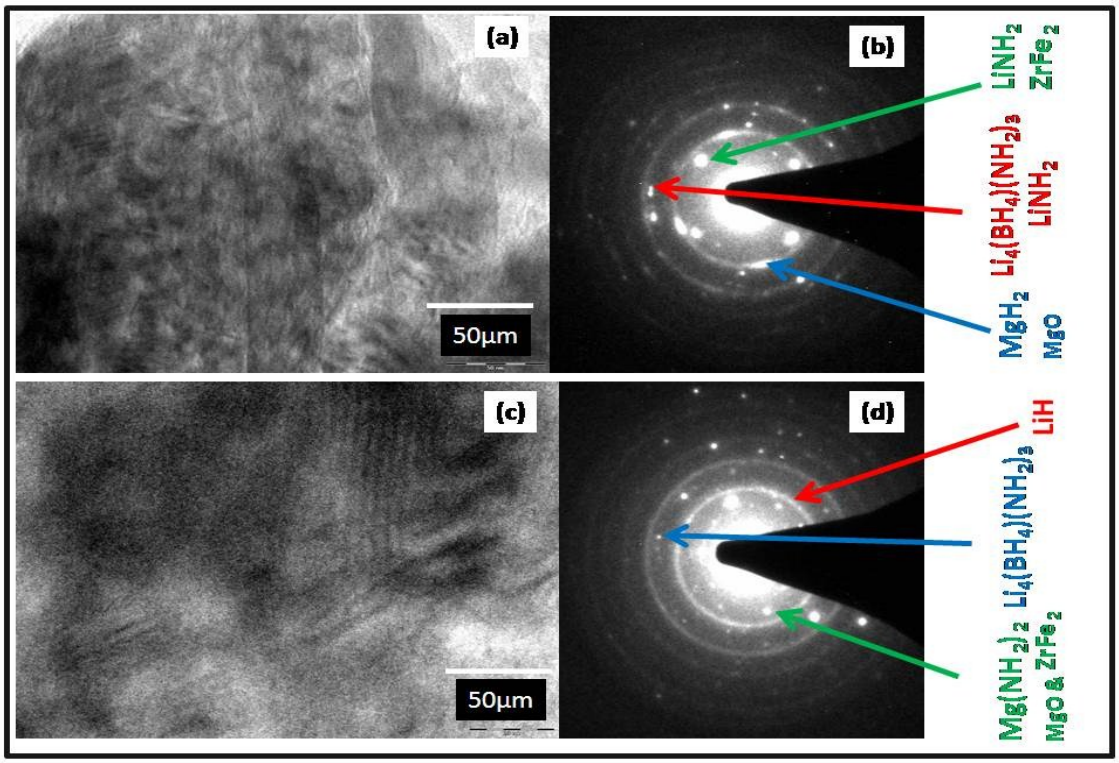

Figure S4 Transmission Electron Micrograph of (a) L-M-B-Z sample (b) Selected area diffraction pattern (SAED) of L-M-B-Z sample (c) After cycling TT L-M-B-Z (d) Selected area diffraction pattern (SAED) of after cycled TT L-M-B-Z sample.