Electronic Supplementary Information

A Liquid-Based Eutectic System: LiBH₄·NH₃-nNH₃BH₃ with High Dehydrogenation Capacity at Moderate Temperature

Yingbin Tan,^{a,b} Yanhui Guo,^b Shaofeng Li,^b Weiwei Sun,^b Yihan Zhu,^c Qian Li,^{*a} Xuebin Yu^{*b}

Hydrogen desorption kinetics

Generally, the rate equation of kinetics for chemical reaction is expressed as follows

$$rate = \frac{d\alpha}{dt} = k(T)f(\alpha)$$
(1)

in which α is the extent of the reaction ranging from 0 when the reaction starts to 1 when it completes, *t* is the time, *T* is the absolute temperature, k(T) is a temperature-dependent reaction rate constant, and $f(\alpha)$ is a term for the reaction rate which is dependent on the reaction mechanism including the nucleation and nuclei growth, the chemical reaction, the geometrical contraction, the diffusion, and the reaction order models based on the different geometry of the particles and the different driving forces. Many different rate expressions have also been derived from these mechanisms. Several most commonly used mechanisms are listed in previous work.^[S1-S4]

Based on experimental data of hydrogen desorption curves, the reacted fraction α can be calculated and α -*t* dependence is described by integral functions. The α can be calculated by

$$\alpha = \frac{\Delta m}{\Delta m_{\max}} = \frac{\frac{\Delta m}{m_0}}{\frac{\Delta m_{\max}}{m_0}}$$
(2)

where m_0 is the initial weight of the sample, Δm and $\Delta mmax$ are the decrease of hydrogen desorption weight at time t and at the time reaching final equilibrium, respectively. The experimental data of α and t from $\Delta m/m_0-t$ kinetic curves of hydrogen desorption were regressed by the least square method on a computer based on Eq. (1) with different rate expressions. On comparing the slope thus with the theoretical slopes, the reaction mechanism can be determined. It is generally preferable to use methods of analysis which produce a linear plot rather than the method of comparing with theoretical curves. The value of the linear slope of an acceptable model should be very close to 1. Then, the rate constant k can be obtained. The larger the rate constant is, the faster the reaction rate is. Finally, from the Arrhenius plot of ln k versus 1/T, one may obtain the slope and intercept of the straight line for (-E/R) and the pre-exponential factor, respectively.

On the other hand, Chou et al. have proposed a method ^[S5] to express the reacted fraction of hydriding/dehydriding reaction as an explicit function of time (t), temperature (T), hydrogen partial pressure (P_{H2}) and particle radius (R_0) under some approximate but reasonable assumptions. A new concept, the "characteristic reaction time" of substance, was introduced to study and compare the kinetics of hydriding/dehydriding reactions. When the rate-controlling step is the diffusion of hydrogen, Chou et al. have proposed following formulae

$$\alpha = 1 - \left(1 - \sqrt{\frac{t}{t_{c(d)}}}\right)^3$$
(3)

When the rate-controlling step is not diffusion, Chou et al. have offered a series of other formulae.^[S6] For instance, when the rate-controlling step is the surface penetration, the relationship between the hydriding reacted fraction ξ and time *t* can be expressed as

$$\alpha = 1 - \left(1 - \frac{t}{t_{c(sp)}}\right)^{3}$$
(4)

The characteristic reaction time (t_c) can be calculated by fitting experimental data with Eq. (3) or Eq. (4) using the least square method. The corresponding squared correlation coefficient, r^2 , reflects the level of agreement between fitting curve and experimental data. A larger r^2 indicate a better agreement between the fitting results and experimental data. The rate-controlling step and the activation energy of hydrogen desorption were determined using the equations proposed by Chou et al..^[S5, S6]



Fig. S1 A summary of dehydrogenation purities of LiBH₄·NH₃-nAB.



Fig. S2 a) EATPD and TPD results of gas evolution for $LiBH_4 \cdot NH_3$ with a heating rate of 5 °C·min⁻¹. It shows that the NH₃ can be eliminated totally before 250 °C. Therefore, the EATPD experiments were conducted before 250 °C. b) EATPD Schematic

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry This journal is O The Royal Society of Chemistry 2011



Fig. S3 XRD patters at 0 °C for LiBH₄·NH₃-3AB, LiBH₄·NH₃-2AB and LiBH₄·NH₃-AB. The neat AB and LiBH₄·NH₃ were also measured for comparison.



Fig. S4 TPD results for AB and LiBH₄/AB with a heating rate of 5 °C ·min⁻¹.

As given in Fig. S4, the TPD results of hydrogen release for LiBH₄/AB were compared with that of neat AB. It shows that the gas evolution onset temperature for the LiBH₄/AB system was significantly lowered compared to neat AB, whereas the hydrogen release is comparable to that of the neat AB, suggesting that the gas evolution was mainly caused by the AB component.



Fig. S5 The XRD patterns for a) LiBH₄·NH₃-AB dehydrogenated to 250 °C, b) LiBH₄·0.4NH₃, c) LiBH₄·0.7NH₃

As given in Fig. S5, the XRD spectrum of dehydrogenated $LiBH_4 \cdot NH_3$ -AB sample was compared with $LiBH_4 \cdot 0.4NH_3$. The overall agreement is good, however some deviation is observed in the relative intensities that may be due to variations in the amount of ammonia. Meanwhile, the peaks distribution of $LiBH_4 \cdot 0.7NH_3$ spectrum is essentially changed compared to those of $LiBH_4 \cdot 0.4NH_3$, indicating that different *x* values corresponding to different phases in the $LiBH_4 \cdot NH_3$.



Fig. S6 MS results for the LiBH₄·NH₃-AB, LiBH₄·NH₃-2AB and LiBH₄·NH₃-3AB measured at 10 $^{\circ}$ C·min⁻¹ to 250 $^{\circ}$ C.

As given in Fig. S6, the decomposition temperature for the LiBH₄·NH₃/AB system was ca. 110 $^{\circ}$ C, and a small amount of volatile by-products (borazine and diborane) starts to release from ca. 125 $^{\circ}$ C. There is a steady decrease in ammonia release with the increasing ratio of AB, whereas the release of diborane and borazine is in a growing trend. Furthermore, a careful examination of the MS results indicated that the evolution of ammonia and hydrogen is ahead of the borazine and diborane release.



Fig. S7 The isothermal dehydrogenation properties of LiBH₄·NH₃-3AB sample at 110 $^\circ$ C.



Fig. S8 XRD patterns of LiBH₄ NH₃-3AB-Na samples before and after dehydrogenation at 250 °C.

As given in Fig. S8, there are sharp patterns assigned to NaBH₄ patterns according to PDF card (#09-0386). This suggests that the DADB is one of the chemical species featured in the LiBH₄·NH₃-3AB mixtures, suggesting that the polar reaction environments of AB may promote formation of more reactive chemical species, which will facilitate B-H···H-N interactions between LiBH₄·NH₃ and AB, to enhance the dehydrogenation of the LiBH₄·NH₃/AB system. Meanwhile, some unknown phase is observed in the LiBH₄·NH₃-3AB-Na samples, which may be PAB formed by reaction (1):

 $xNa + xBH_2(NH_3)_2BH_4 = xNaBH_4 + (NH_2BH_2)_x + 1/2xH_2 + xNH_3$ (1)

References

S1 Q. Li, K. C. Chou, Q. Lin, L. J. Jiang, F. Zhan, Int. J. Hydrogen Energy 2004, 29, 843-849.
S2 J. Liu, X. Zhang, Q. Li, K. C. Chou, K. D. Xu, Int. J. Hydrogen Energy 2009, 34, 1951-1957.
S3 Y. F. Liu, K. Zhong, K. Luo, M. X. Gao, H. G. Pan, Q. D. Wang, J. Am. Chem. Soc. 2009, 131, 1862-1870.
S4 J. Lu, Young Joon Choi, Zhigang Zak Fang, Hong Yong Sohn, E. Rönnebro, J. Am. Chem. Soc. 2010, 132, 6616-6617.
S5 K. C. Chou, Q. Li, Q. Lin, J. Li, K. D, Xu, Int. J. Hydrogen Energy 2005, 30, 301-309.
S6 K. C. Chou, K. D. Xu, Intermetallics 2007, 15, 767-777.