Effect of LiH on the Dehydriding Property of α-AlH₃ Composite

C W Duan[1,*], J Zhang[2], Y L Zhang[1] and J L Ma[3]

[1] Department of Environmental Science and Engineering, North China Electric Power University, Baoding, 071003, China
[2] Department of Computed Tomography and Magnetic Resonance Imaging, Baoding First Center Hospital/First Aid Center, Baoding, 071003, China
[3] School of Information Science and Engineering, Hebei University of Science and Technology, Shijiazhuang, 050018, China

Corresponding author and e-mail: C W Duan, Duancw@ncepu.edu.cn

Abstract. As a promising hydrogen storage composite, the a-AlH₃/LiCl nano-composite was prepared by mechanochemical synthesis method. However, so far there is no investigation on the dehydriding property of this composite. In present work, the hydrogen desorption property of this composite is investigated systematically. When heating temperature goes from 80 to 140 °C, the isothermal desorption measurements show that 9.93 wt% of hydrogen is released from the composite and the kinetic of the dehydrogenation improved with the temperature raised. Moreover, thermal analysis by differential scanning calorimeter (DSC) is used to research the de-hydriding process of the a-AlH₃/LiCl nano-composite, from which the composite composes one step with the direct decomposition of the α phase. With the LiH introduced into the AlH₃/LiCl nano-composite, the dehydrogenation measurements reveal that the de-hydriding kinetics of this system was also improved. According to the DSC results, it is found that the LiH addition can reduce the activate energy of the de-hydriding reaction.

1. Introduction

In order to seek a new and green energy source, hydrogen is regarded to be a perfect carrier for energy storage, transportation application and the application of hydrogen-fueled cells due to its unique feature of non-toxicity, high energy density and promising performance in fuel cells [1]. In recent years, on-board hydrogen storage posed considerable technical challenges that could be detrimental to the application of fuel cells [2]. Therefore, a lightweight, effective and high capacity hydrogen storage material should be developed for hydrogen storage [3]. Among the various light hydrides, AH₃ (alane) with a higher gravimetric hydrogen capacity exceeding 10 wt%, a lower desorption temperature (100-200 °C) and a minor dehydriding enthalpy, is acknowledged as a fascinating material, and attracted more and more attentions for its potential as a hydrogen storage candidate [4].

It is well known that the non-solvated AlH₃ with seven variations in its crystal structures, such as $α, α', β, γ, δ, ε$ and $ζ$ phase, were firstly synthesized by the direct reaction of LiAlH₄ and AlCl₃ in diethyl ether solvent [5]. Based on the thermodynamic calculation, it is deduced that the $α$ and other

phase of AlH_3 can spontaneously decompose at 298 K [6]. But, it was verified by Graetz that the decomposition of AlH_3 polymorphs is still not feasible at room temperature mainly due to the effect of dehydriding kinetics [7]. Among the seven AlH_3 polymorphs, the unit cell, lattice parameters and bridge bonds of the α phase were determined by Turley et. al. in 1969, from which only one type of corner connected AlH_6 octahedra consist in this structure [8]. In view of the above structural analysis, α-AlH_3 is more stable than other polymorphs. According to the formation enthalpy and formation entropy of α phase calculation, the Gibbs formation energy for α phase at 300 K can be obtained with a value of 31 KJ/mol H_2 [9]. Therefore, it can be concluded from the above thermal analysis that α-AlH_3 is recognized to be more stable than other phase.

It was also verified by Liu that the initial dehydriding temperature of the fresh γ-AlH_3 is still to be about 130 °C [2], which probably hinders the application of AlH_3 as an hydrogen storage material. A promising approach proposed by Gutowska that the nano-sized metal hydride could increase the dehydriding kinetics without doping of catalyst [10]. Thus, the searching group focused on the improving desorption kinetics with a ball milling method [11]. Orimo et. al. Also found that only milling the as-prepared AlH_3 could reduce the dehydriding temperature and accelerate the desorption rates [9]. But, their works were mainly focus on the thermodynamics of milled AlH_3, not the dehydriding reaction kinetics. Similarly, Graetz reported that an fresh nano-sized AlH_3 synthesized by wet chemical method also exhibits an desirable decomposition temperature less than 100 °C [12], and have a high H_2 yield which can approach the theoretical hydrogen content of AlH_3 (10 wt.%) without needing furthermore ball milling or mixing as-prepared AlH_3 with small levels of the alkali metal hydrides [7]. Nevertheless, the above mentioned methods are not perfect due to complexity and extremely sensitive during the process of synthesizing nano-sized AlH_3. Namely, an additional approach such as ball milling was performed to product nano-sized hydride from the obtained AlH_3. Furthermore, the desolvating process for removing large quantities of organic solvents from the solvates is uneconomical and hazardous.

Recently, the mechanochemical method is considered to be both green and economical powerful tool to obtain metal hydrides [13]. This mechano-chemical method was later investigated by research group that employed a desirable way to synthesize nano-sized AlH_3 [14]. Nevertheless, as a promising hydrogen storage media, the dehydriding property of as-milled AlH_3 composite was still not investigated and discussed systematically. More effort should be focus on the dehydriding kinetics of a-AlH_3 nano-composite. In our previous work, the a-AlH_3/LiCl nano-composite was successfully prepared by a liquid state reaction between LiH and $AlCl_3$ [15]. In present study, the de-hydriding process and de-hydriding kinetics of this nano-composite is thoroughly investigated.

2. Experimental

The a-AlH_3/LiCl nano-composite was firstly prepared by liquid state reaction milling with LiH, $AlCl_3$ and ionic liquid [15]. To investigate the effect of LiH on the a-AlH_3 dehydriding property, the excessive LiH (5 mol %) was added into reaction system directly. The mixed powder was put in a ball-milling canister. Ball milling was performed via a planetary-type QM-SP4 device attached to 500 cm^3 ball-milling canisters. During the mechanochemical reaction, hydrogen pressure in the vial was kept above 5 MPa. The as-milled composite was eventually formed after ball milling.

Isothermal and Non-isothermal dehydriding tests were carried out on a home-made special vacuum apparatus made reactor. The a-AlH_3/LiCl nano-composite was loaded into a stainless holder. In order to investigate dehydriding kinetics of composite systemically, the as-milled samples were powdered at different temperatures of 80, 120 and 140 °C. The time required for the full dehydriding reaction was fixed at 5,000 s, respectively. During the temperature programmed desorption (TPD) process, the rate of heating temperature as well as the vacuity in closed special equipment were controlled by a computer and monitored in situ with digital vacuum gauges. To investigate the dehydriding process of the a-AlH_3 nano-composite, the TPD measurements were performed from 40

to 240 ℃ with a heating rate of 3 ℃/min. The hydrogen content desorbed from the composite was calculated in terms of the vial vacuum change. Based on the stoichiometric weight of AlH$_3$ calculated by the chemical reaction, the dehydriding curves of as-milled AlH$_3$/LiCl and LiH/AlH$_3$/LiCl nano-composite could be obtained. Thermal analysis was studied by differential scanning calorimetry (DSC) on a DSC METTLER TOLEDO instruments. In order to prevent the sample form oxidizing, the samples was sealed into a crucible (constructed from Al) in glove box and quickly transferred to the instrument in T-zero pans. During the measurement, the argon was flowed at 20 mL/min to minimize the sample exposure to air. Subsequently, the samples were heated from 40 to 240 ℃ at various rates of 3, 5, 10, 15 ℃/min, respectively. It is noted that the as-milled products which mixed with ionic liquid were filtrated and dried in a vacuum before de-hydriding measurement.

3. Results and Discussion
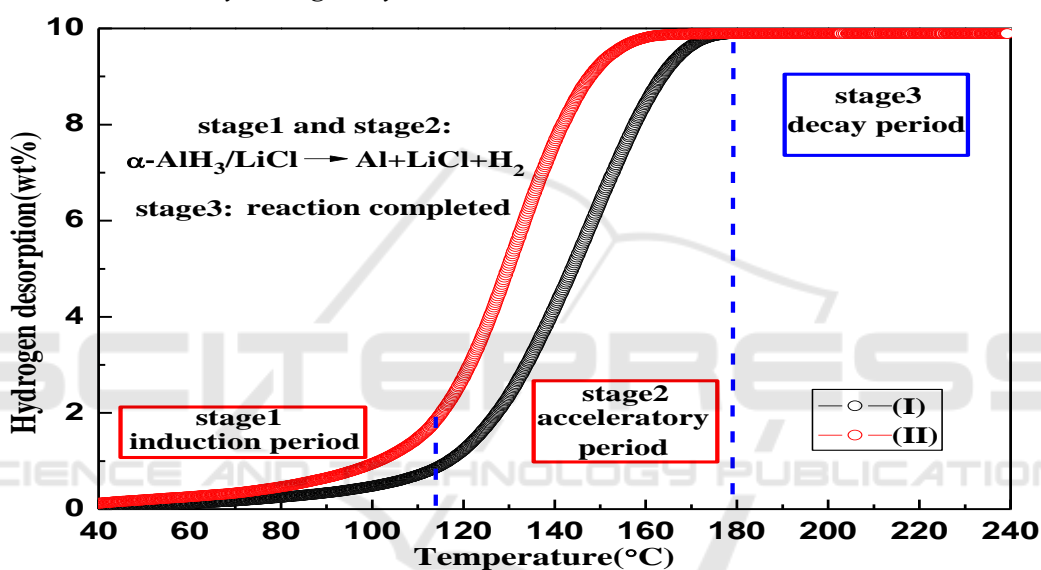
3.1. Non-isothermal dehydriding analysis

Figure 1. TPD curves of (I) as-milled *a*-AlH$_3$/LiCl nano-composite, (II) *a*-AlH$_3$/LiCl nano-composite doped with LiH.

The non-isothermal desorptions of the *a*-AlH$_3$/LiCl nano-composite and the same product with LiH addition are shown in Figure 1. The curves of non-isothermal desorptions are investigated by the temperature-programmed-desorption (TPD) measurements from 40 to 240 ℃ with a heating rate of 3 ℃/min. It is shown from Figure 1 that the obtained nano-composite starts to release hydrogen approximately to be 60 ℃ and subsequently follows a slow desorption process between 60 and 115 ℃. The hydrogen content released from the composite is just 0.86 wt % after the temperature is gradually increased to 115 ℃. This hydrogen capacity is much lower than the theoretical gravimetric hydrogen capacity of pure AlH$_3$, suggesting that a small proportion of decomposition occurred with a relatively slow heating rate. When the heating temperature is gradually increased to 180 ℃, the desorption process slows down with a maximum hydrogen desorption capacity of 9.93 wt% for the as-milled nano-composite, which is approximately to be the theoretical hydrogen capacity with a value of 10.1 wt%. It can be concluded that the all the AlH$_3$ in this composite decomposed into Al under a higher de-hydriding temperature. Overview the TPD curves of the composites in Figure 1, it is indicated that the hydrogen desorption of the *a*-AlH$_3$/LiCl nano-composite exhibits a three-stage process. Namely, the introduction stage starts at 60 ℃ and ends at 115 ℃, and subsequently an

accelerated period of decomposed process as well as an final stage identified as the decay period. However, it is observed from the curve of (II) in Figure 1 that the de-hydriding rate of *a*-AlH$_3$/LiCl composite was faster than the product without LiH addition. Furthermore, AlH$_3$ doped with LiH presents a more desirable de-hydriding kinetics. This is attributed to the LiH has some effects on the decomposition kinetics of AlH$_3$. These results have good correspondence with the our previous work in which Zn and Zr can accelerate the de-hydriding reaction of AlH$_3$ [16, 17]. Thus, it can be deduced that LiH also can act as an impediment to overgrowth of metal Al and subsequently improve the dehydriding kinetics during the desorption process.

3.2. Isothermal dehydriding property of the a-AlH$_3$/LiCl nano-composite
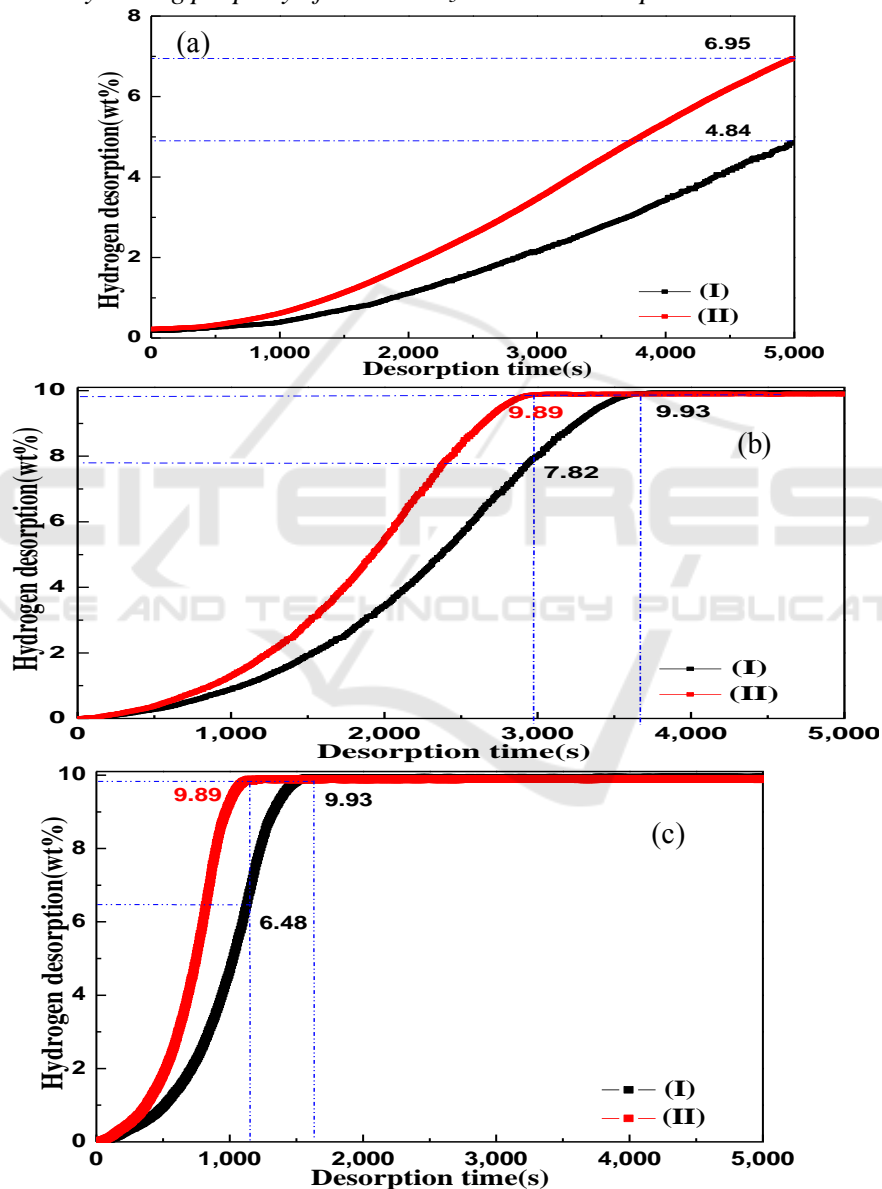

Figure 2. The de-hydriding kinetics curves of (I)*α*-AlH$_3$/LiCl nano-composite and (II) the same composite added with LiH at various temperatures: (a) 80 °C, (b) 120 °C, (c) 140 °C.

To explore the effect of LiH on the synthesis of the α-AlH₃/LiCl composite, Figure 2 shows the curves of dehydriding kinetics of the as-milled α-AlH₃ composite at various temperatures and different time intervals. As can be seen in Figure 2 that the rate of dehydrogenation accelerated as the temperature rose to 140 ℃. Additionally, from the curves for dehydrogenation reaction, it can be conjectured that LiH has remarkable effect on the dehydrogenation reaction of the α-AlH₃/LiCl nano-composite. When the de-hydriding temperature is fixed at 80 ℃ for 5,000 s, it can be seen from the Figure 2(a) that the hydrogen desorption content of as-milled product reached merely 4.84 and 6.95 wt% respectively, indicating that the dehydriding reaction was still not complete under this condition. Compared with the AlH₃/LiCl composite without adding LiH, AlH₃ has a significant advantage on dehydriding property with the same hydrogen content at 80 ℃ for 3,736 s. Although the dehydriding curve exhibited an undesirable property, the as-milled product still have an advantage in de-hydriding properties compared with the much lower hydrogen content of 1.9 wt% derived from the as-milled AlH₃ which fully decomposed from room temperature to 200 ℃ [14]. Furthermore, the value described above, was higher than the 0.48 wt% hydrogen content of crude α-AlH₃ measured by Graetz. et. al.[3, 6, 7].   By increasing the reaction temperature to 120 ℃ for 3,000 s, the hydrogen content of α-AlH₃/LiH composite increased rapidly to 9.89 wt%, suggesting that almost all the AlH₃ decomposed, much more than at lower temperature. Even dopped with LiH, it was demonstrated by Sandrock that only 4 wt % H₂ can be obtained from the AlH₃/LiH composite in the the first four hours [18]. Furthermore, the same hydrogen content could be obtained by heating the reaction mixture at 140 ℃ for the 1,140s, which implied that the dehydrogenation rate was clearly accelerated by increasing the temperature. It is obvious that the AlH₃ added with LiH has a more desirable dehydriding dynamics. Consequently, the LiH probably come into play with the decomposition kinetics of α-AlH₃ and can accelerate the de-hydriding reaction of α-AlH₃. Although fresh synthesized nanoscale α-AlH₃ has an advanced dehydrogenation property, it was reported by Graetz that fully decomposed time at 138 ℃ can be achieved even within 1,800s [12]. Therefore, it can be concluded that the α-AlH₃ nano-composite doped with LiH exhibits an excellent advantage in de-hydriding property.

3.3. The de-hydriding kinetics of the a-AlH₃/LiCl nano-composite

In order to gain an deep insight into the de-hydriding process of the α-AlH₃/LiCl/LiH nano-composite, further supporting evidence can be obtained from the DSC curves in Figure 3. Figure 3(a) shows DSC curves of as-milled α-AlH₃ composite added with LiH at several heating rates. It is obvious that the desorption curves of the composite added with LiH still have a similar peaks with that of un-doped composite. The whole DSC curves contain only one endothermic peak at a elevated temperature of 40-240 ℃. This endothermic peak derives from α-AlH₃ decomposition is consistent with Liu report [2]. It was found that the endothermic peak between 80 and 190 ℃ is assigned to the de-hydriding reaction of the α phase [2]. This indicates that no new phase was formed in the product. Namely, α-AlH₃ can not react with LiH during the de-hydriding process. Based on the above non-isothermal analysis, the corresponding de-hydriding temperature of α-AlH₃ is remarkably reduced with the LiH added into the composite. Thus, it can be deduced that the LiH have some effects on the decomposition kinetics of α-AlH₃. To determinate the value of apparent activation energies (Ea) for this dehydriding process, the desorption kinetics of the α-AlH₃/LiCl nano-composite was studied by using the Kissinger's method. Moreover, the relationship among the activation energy (Ea), the heating rate (c), and the peak temperature of de-hydriding (T_P) in the DSC curve can be formulated by following Kissinger's equation:

$$\text{Ln} (c/T_p^2) = - (E_a/RT_p) + A \qquad (1)$$

Figure 3(b) shows the activation energy of the de-hydriding reaction based on parameters obtained from DSC measurements. The apparent activation energy for the hydrogen desorption of α-

AlH$_3$ in the composite were estimated to be 52.9 KJ/mol, which are slightly lower than that of the as-milled AlH$_3$/LiCl nano-composite without LiH addition (56.8 KJ/mol) [15]. This value is also lower than result reported by Gabis who found that the apparent activation energy of the dehydrogenation of α-AlH$_3$ is 104 KJ/mol [19]. This decrease in the kinetic barrier is contribute to the remarkable improvement in the hydrogen desorption kinetics, and the decrease in the activation energy can describe the above TPD and DSC results vigorously, from which the α-AlH$_3$/LiCl nano-composite added with LiH has a more desirable de-hydriding kinetics.
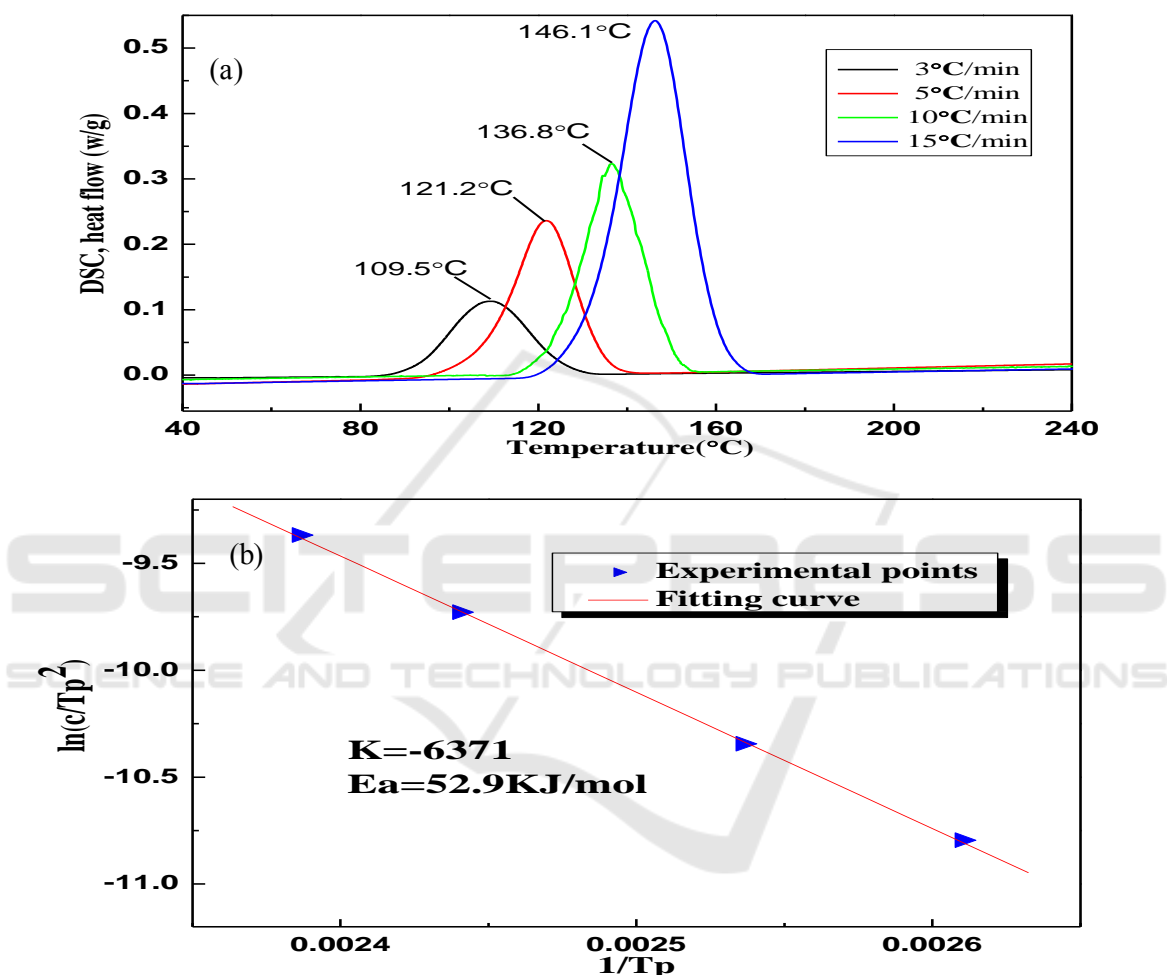

Figure 3. (a) DSC curves of the α-AlH$_3$ nano-composite doped with LiH in temperature ranges from 40 to 240 ℃, (b) The apparent energy for the decomposition obtained from DSC measurements.

4. Conclusions

The α-AlH$_3$/LiCl nano-composite which was prepared by mechanochemical methods releases about 9.9 wt% of hydrogen in the temperature of 40-240 ℃. Combining the DSC analysis, the de-hydriding process of the α-AlH$_3$ nano-composite was found, that is, the obtained α-AlH$_3$ dehydride directly during the dehydriding process. Moreover, the α-AlH$_3$ nano-composite doped with LiH exhibits an excellent advantage in de-hydriding property. With the LiH added into composite, the activation energy of de-hydriding of α-AlH$_3$ was reduced from 56.8 to 52.9 kJ/mol. Thus, it can be deduced that LiH can remarkably improve the de-hydriding kinetics of the α-AlH$_3$ nano-composite.

References

[1]   Contestabile M, Offer G J, Slade R, Jaeger F and Thoennes M 2011 *Energ. Environ. Sci.* **4** 3754-72.

[2]   Liu H, Wang X, Dong Z, Cao G, Liu Y, Chen L and Yan M 2013 *Int. J. Hydrogen Energy* **38** 10851-56.

[3]   Graetz J 2009 *Chem. Soc. Rev.* **38** 73-82.

[4]   Banach E M, Stil H A and Geerlings H 2012 *J. Mater. Chem.* **22** 324-7.

[5]   Brower F M, Matzek N E, Reigler P F, Rinn H W, Roberts C B, Schmidt D L and Terada K 1976 *J. Am. Chem. Soc.* **98** 2450-3.

[6]   Graetz J and Reilly J J 2006 *J. Alloys. Compd.* **424** 262-5.

[7]   Graetz J and Reilly J J 2005 *J. Phy. Chem. B* **109** 22181-5.

[8]   Turley J W and Rinn H W 1969 *Inorg. Chem.* **8** 18-22.

[9]   Orimo S, Nakamori Y, Kato T, Brown C and Jensen C M 2006 *Appl. Phys. A* **83** 5-8.

[10]   Gutowska A, L Li, Shin Y, C M Wang, X S Li, Linehan J C, Smith R S, Kay B D, Schmid B, Shaw W, Gutowski M and Autrey T 2005 *Angew. Chem. Int. Ed.* **44** 3578-82.

[11]   Huot J, Pelletier J F, Lurio L B, Sutton M and Schulz R 2003 *J. Alloys Compd.* **348** 319-24.

[12]   Graetz J, Reilly J J, Kulleck J G and Bowman R C 2007 *J. Alloys. Compd.* **446** 271-5.

[13]   Fernandez J A, Aguey-Zinsou F, Elsaesser M, Ma X Z, Dornheim M, Klassen T and Bormann R 2007 *Int. J. Hydrogen Energy* **32** 1033-40.

[14]   Gupta S, Kobayashi T, Hlova I Z, Goldston J F, Pruski M and Pecharsky V K 2014 *Green Chem.* **16** 4378-88.

[15]   C W Duan, L X Hu and J L Ma 2018 *J. Mater. Chem. A* **6** 6309-18.

[16]   C W Duan, L X Hu and Y Sun 2015 *RSC Adv.* **5** 17104-8.

[17]   C W Duan, L X Hu Y Sun and Z P Wan 2016 *RSC Adv.* **6** 74215-24.

[18]   Sandrock G, Reilly J and Graetz J 2005 *Appl. Phys. A* **80** 687-90.

[19]   Gabis I, Dobrotvorskiy M and Evard E 2011 *J. Alloy. Compd.* **509** S671-4.