

HYDROGEN STORAGE ON LiNH₂/LiAlH₄/MgH₂ WITH TiO₂, Ti AND CNTs

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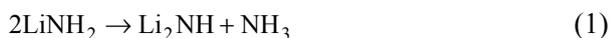
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Introduction

Solid hydrogen storage materials have been investigated as hydrogen carriers due to their safety in hydrogen applications. Recently, amide-based materials have been focused due to their high H₂ capacity, particularly LiNH₂ (8.7 wt% H₂) [1]. However, its slow kinetics and high stability are big challenges, which have to be overcome [2]. Moreover, one of the issues with the amide-based materials is the possibility of NH₃ generation during the decomposition of LiNH₂, which impairs the performance of the catalyst in PEM fuel cell and loses the storage materials itself. Eq. (1) shows the decomposition of LiNH₂ and evolution of NH₃ at 300°C.

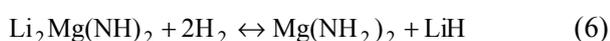
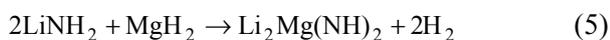


Eq. (2) shows the reaction of LiNH₂ and LiH, which can suppress the release of NH₃ and the products from the reaction contain only H₂ and Li₂NH [3].



Another metal hydride that has a potential to suppress NH₃ is LiAlH₄. The decomposition of LiAlH₄ produces both LiH and H₂ as shown in Eqs. (3) and (4). It releases H₂ at low temperature, 150-160°C and releases hydrogen about 5.3 wt% H₂ [4].

It was found that an increase in the kinetics and destabilization of LiNH₂ can be accomplished by partial substitution of LiNH₂ by Mg. That resulted in the decrease in the H₂ desorption temperature [5]. The dehydriding/hydrating reactions of the LiNH₂ and MgH₂ system are shown in Eq. (5).



Moreover, it was proposed that Li₂Mg(NH)₂ and Mg(NH₂)₂ would act as the reversible phase in the reaction as shown in Eq. (6) [6].

There have been reports that magnesium hydride (MgH₂) can suppress NH₃ released from nitrogen-containing hydrides. MgH₂ also has high hydrogen capacity. Thus, MgH₂ and LiH seem to be good compounds to prevent NH₃ emission and to improve the reversible hydrogen capacity of LiNH₂ [7].

To further prevent the NH₃ ammonia released and improve the H₂ desorption of LiNH₂, in this study, the investigation of adding LiAlH₄ and MgH₂ into LiNH₂ was carried out. Moreover, effects of TiO₂, Ti, and CNTs in the mixture on the reaction were also investigated.

Results and the discussion

Figure 1 shows the mass spectra of NH₃ emission from the mixture of LiNH₂ mixed with LiAlH₄ and MgH₂.

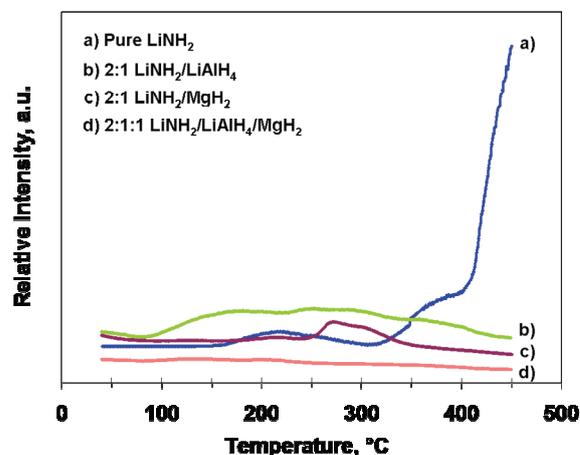


Fig. 1. Mass spectra of ammonia ($m/z = 17$): a) Pure LiNH₂, b) 2:1 LiNH₂/LiAlH₄, c) 2:1 LiNH₂/MgH₂, and d) 2:1:1 LiNH₂/LiAlH₄/MgH₂.

It can be noticed that mixing LiNH₂ with LiAlH₄ or MgH₂ (Figures 1b and 1c) can decrease the NH₃ emission during the decomposition of the hydride while the mixed hydrides of LiNH₂/LiAlH₄/MgH₂ (Figure 1d) completely suppress the NH₃ emission from the hydride system.

The results on hydrogen desorption of LiNH₂/LiAlH₄/MgH₂ with TiO₂, Ti, and CNTs are shown in Figure 2. The mixture doped with TiO₂

and CNTs shows the higher amount of released H₂ than the undoped mixture. And doping with CNTs resulted in the highest amount of H₂ 3.9 wt% H₂. In contrast, the mixture doped with Ti does not show any significantly improvement from the undoped mixture.

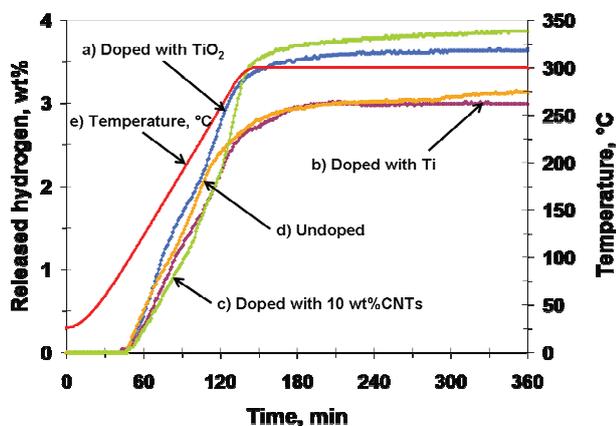


Fig. 2. Hydrogen desorption profile of LiNH₂/LiAlH₄/MgH₂: a) doped with TiO₂, b) doped with Ti, c) doped with CNTs, d) undoped and e) temperature.

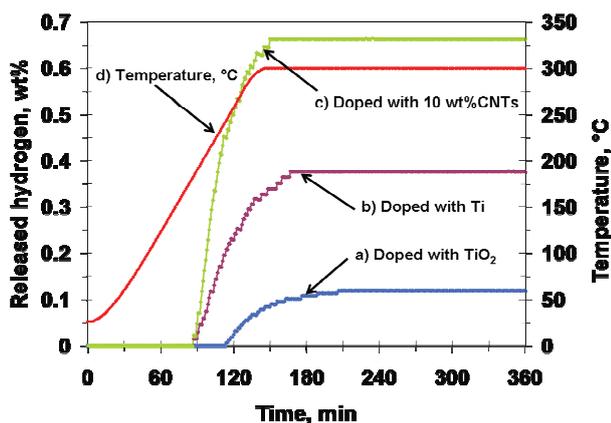


Fig. 3. Subsequent desorption profile of LiNH₂/LiAlH₄/MgH₂: a) doped with TiO₂, b) doped with Ti, c) doped with CNTs and d) temperature.

Figure 3 clearly reveals that the mixture doped with CNTs can re-absorb hydrogen about 0.66 wt%, which is higher than that doped with TiO₂ and Ti.

The XRD result in Figure 4 show that there are LiH peaks, indicating the decomposition of LiAlH₄ after the milling. After the H₂ desorption, the products consist of Mg₃N₂, LiMgN, and Mg₃Al₃N₅. In the case of the H₂ re-absorption, small peaks of Mg(AlH₄)₂ and Mg(NH₂)₂ appear in the re-absorbed products, which are the reversible phases in the mixture [6].

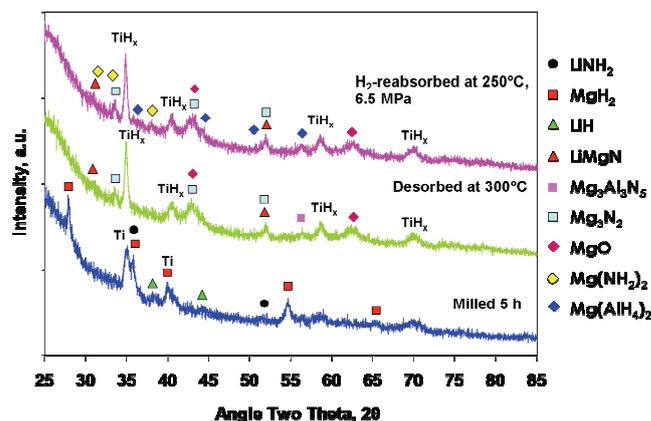


Fig. 4. XRD patterns of LiNH₂/LiAlH₄/MgH₂ doped with Ti.

Conclusions

The NH₃ emission from the decomposition reaction of LiNH₂ was suppressed by adding LiAlH₄ and MgH₂. Moreover, doping with TiO₂, Ti, and CNTs also lowered the decomposition temperature and accelerated the H₂ desorption of the mixed metal hydrides (LiNH₂/LiAlH₄/MgH₂). In addition, the H₂ re-absorption ability of LiNH₂/LiAlH₄/MgH₂ was improved by doping with CNTs, which exhibited the best performance in the reversible H₂ capacity, 0.66 wt%.

References

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