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Improved dehydrogenation cycle performance of the $1.1MgH_2$-$2LiNH_2$-$0.1LiBH_4$ system by addition of $LaNi_{4.5}Mn_{0.5}$ alloy

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Abstract: The isothermal desorption kinetics of the $1.1MgH_2$-$2LiNH_2$-$0.1LiBH_4$ system were improved by addition of $LaNi_{4.5}Mn_{0.5}$ alloy. The hydrogen desorption peak temperature of the sample containing $LaNi_{4.5}Mn_{0.5}$ reduced by approximately 5 K and the activation energy reduced by 9%. The results of isothermal dehydrogenation kinetics analysis implied that the isothermal desorption process at initial stage was controlled by the phase boundary mechanism. Moreover, the cycle performance of the materials was extended. The growth and agglomeration of the sample particles caused the deterioration of kinetics during de-/hydrogenation cycles, and then resulted in an incomplete desorption/absorption reaction which were responsible for the capacity fading. The cracking and pulverization of $LaNi_{4.5}Mn_{0.5}$ alloy had an obvious effect on preventing the composites aggregating, and the fine alloy particles could enhance the catalytic effect of the alloy, thus effectively offsetting part of the deterioration of kinetics caused by particles growth.

Keywords: hydrogen storage materials; Li-Mg-B-N-H hydride; $LaNi_{4.5}Mn_{0.5}$; cycle performance; rare earths

Hydrogen is a green and efficient energy carrier, which is abundant and environmentally benign. One of key issues that limit hydrogen energy application is efficient storage of hydrogen[1]. Nowadays, many efforts have been made for development of new hydrogen storage materials worldwide[2–8]. Among the studied materials, the Li-Mg-N-H system comprised of LiH and $Mg(NH_2)_2$ or $LiNH_2$ and MgH_2, exhibits good reversibility at moderate operation temperatures and a relatively high capacity of 5.6 wt.%. It is therefore regarded as a promising candidate for on-board application[9]. This system can dehydrogenate under 0.1 MPa at 363 K by thermodynamic calculation[9]. However, a rather high kinetics barrier of hydrogen sorption has been identified, which restricts its application. A variety of dopants, KH, KOH, KF, lithium halides, RbF, NaOH, LaH_3, VCl_3, $TiCl_3$, TaN, TiN, Li_3AlH_6, $Ca(BH_4)_2$, $Mg(BH_4)_2$, $LiBH_4$, were investigated to improve the kinetic properties[10–26]. The alkali-metal compounds have been proved to be one of the most effective additives[10–18]. The hydrogen storage properties of $Mg(NH_2)_2$-2LiH were significantly enhanced by adding a small amount of KH[10–12]. The dehydrogenation peak temperature was lowered from 459 K for the $Mg(NH_2)_2$-2LiH sample to 405 K for the $Mg(NH_2)_2$-1.9LiH-0.1KH sample[10]. However, the positive effects of K-based additives disappear when the hydrogen release and uptake of the KF-added $Mg(NH_2)_2$- 2LiH samples are performed at higher temperatures (>473 K)[14,15]. It was found that metal borohydrides, such as $Mg(BH_4)_2$, $Ca(BH_4)_2$ and $LiBH_4$, were another sort of effective dopants for improving the reaction kinetics of both dehydrogenation and hydrogenation of the Li-Mg-N-H system[23–26]. Yang et al. demonstrated that by starting with the mixture MgH_2+$LiNH_2$+$LiBH_4$, the desorption reaction could proceed at lower temperatures and with significantly enhanced kinetics[26]. Via an in- depth exploration of the ternary mixture, a self-catalyzing reaction has been found, which improved the low temperature kinetics of the reversible reaction between $Li_2Mg(NH)_2$ and $2LiH$+$Mg(NH_2)_2$[27]. The effect of the stoichiometry on the hydrogen storage property of this ternary complex hydride system has also been investigated[28,29].

To improve the hydrogen storage behavior of the Li-Mg-B-N-H system, various nanosized metals (Ni, Co, Fe, Cu, Mn) were added to this system. It was found that the additives of Co and Ni lowered the hydrogen releasing temperature at least 75–100 K in the major hydrogen decomposition step, while other additives acted as catalysts and increased the rate at which hydrogen was released[30]. With the addition of $ZrCoH_3$, significant improvements in the hydrogen absorption/desorption properties of $2LiNH_2$-$1.1MgH_2$-$0.1LiBH_4$ composite have been achieved[31,32].

However, the researches on cycle performance of the Li-Mg-B-N-H system were rarely reported. As men-

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tioned above, the hydrogen storage properties of the Li-Mg-N-H system could be improved by adding LaH_3[19]. Here, we studied the effect of the $LaNi_{4.5}Mn_{0.5}$ alloy on hydrogen sorption properties of the $2LiNH_2$-$1.1MgH_2$-$0.1LiBH_4$ composite. $LaNi_{4.5}Mn_{0.5}$ alloy is hard, brittle and easy to pulverize. The cycle performance and mechanism for hydrogen capacity fading was investigated.

1 Experimental

The starting materials $LiNH_2$ and $LiBH_4$ (95% purity, Sigma-Aldrich) were used as received without purification. The MgH_2 was home-made by ball-milling Mg powder under 4 MPa H_2 pressure for 60 h, and then it was rehydrogenated for three times to obtain high-purity MgH_2 (>95% purity).

The $LaNi_{4.5}Mn_{0.5}$ intermetallic compound was re-melted three times by magnetic levitation melting under an argon atmosphere. The alloy was annealed in evacuated quartz tubes at 1273 K for 8 h, and then quenched in the water. The annealed alloy was hydrogenated for pulverising to –500 mesh powder under 5 MPa H_2 pressure at ambient temperature.

3 g mixture of MgH_2, $LiNH_2$ and $LiBH_4$ with molar ratio of 1.1:2:0.1 was put into a stainless steel vial for high-energy ball-milling under 4 MPa H_2 pressure using a Spex-8000 apparatus. The weight ratio of stainless steel ball to powder was 20:1 and the total milling time was 36 h. The composite with an addition of 10 wt.% $LaNi_{4.5}Mn_{0.5}$ was prepared by high-energy ball milling $LaNi_{4.5}Mn_{0.5}$ hydride powder and the as-milled Li-Mg-B-N-H powder for 12 h. In order to reduce the amorphous phase produced by ball-milling, the stainless steel balls were replaced with zirconia balls and the weight ratio of ball to powder was 2:1. In case of the alloy with partially amorphous phase, the p-c isotherms differ significantly from the alloy without amorphous phase with an enhancement of solid state solubility and a lowering of the plateau pressure[33].

Isothermal dehydrogenation kinetics were measured using a Sieverts-type apparatus. Approximately 0.5 g of sample was used in each measurement. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 409 unit. About 40 mg of samples were heated at a heating rate of 5 K/min under Ar atmosphere. The gas generated in the heating process was monitored by a mass spectrometer (MS). XRD analysis was carried out by using an X'pert Pro MPD diffractometer with Cu Kα radiation at 40 kV and 40 mA. The IR absorption spectrum was collected in diffuse reflectance infrared Fourier transform mode at a resolution of 4 cm^{-1}, and the sample was mixed with paraffine in an appropriate proportion in order to isolate air. The morphology and element distributions of the composites were measured by a field emission scanning electron microscope (SEM, Hitachi model S4800). All handling procedures in this work were performed in a glove-box filled with purified argon to keep the H_2O and O_2 levels below 1 ppm.

2 Results and discussion

2.1 Effects of $LaNi_{4.5}Mn_{0.5}$ on dehydrogenation kinetics and thermal effects

Desorption isotherms were first measured for comparison of the effects induced by the addition of $LaNi_{4.5}Mn_{0.5}$. Fig. 1 presents hydrogen desorption kinetics curves under 0.1 MPa at 423 K of the Li-Mg-B- N-H system with and without $LaNi_{4.5}Mn_{0.5}$ addition. The dehydrogenation curves indicate that the desorption kinetics are enhanced by mixing 10 wt.% $LaNi_{4.5}Mn_{0.5}$ alloy. It has been found that the hydrogen release capacity is 3.12 wt.% and 3.62 wt.% within 120 min for the Li-Mg-B-N-H sample and the sample with $LaNi_{4.5}Mn_{0.5}$ addition respectively. However, the capacity loss for the sample added with $LaNi_{4.5}Mn_{0.5}$ is exhibited, due to the larger density and the smaller capacity of $LaNi_{4.5}Mn_{0.5}$, compared with the pristine sample of Li-Mg-B-N-H.

Fig. 2(a) shows the DSC curves of the Li-Mg-B-N-H and 10 wt.% $LaNi_{4.5}Mn_{0.5}$ samples which were measured at a heating rate of 5 K/min from 303 to 623 K under argon atmosphere. The exothermic peaks at about 423 K coincide with the metathesis reaction that was observed by Luo et al.[34], which is very close to the results reported by Hu et al.[32].

The broad endothermic peaks in the temperature range of 463–483 K are obviously formed by the superposition of two peaks, which correspond to the two hydrogen desorption reactions reported by Yang et al.[27] in Eqs. (1) and (2) respectively.

$$2Li_4BN_3H_{10}+3MgH_2 \rightarrow 3Li_2Mg(NH)_2+2LiBH_4+6H_2 \quad (1)$$

$$Mg(NH_2)_2+2LiH \rightarrow Li_2Mg(NH)_2+2H_2 \quad (2)$$

$Li_4BN_3H_{10}$ should be formed by the reaction of $LiNH_2$

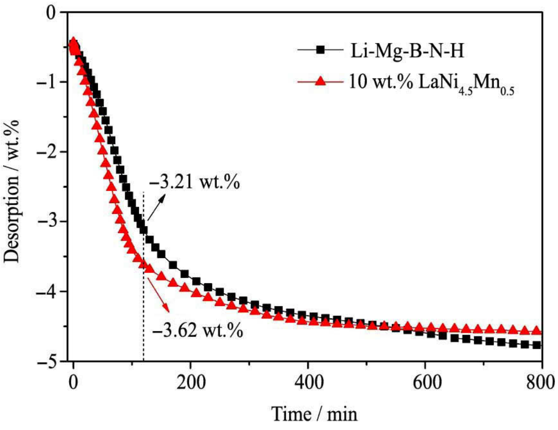

Fig. 1 Hydrogen desorption kinetics curves under 0.1 MPa at 423 K of the Li-Mg-B-N-H sample and the 10 wt.% $LaNi_{4.5}Mn_{0.5}$ added sample