Ternary Amides Containing Transition Metals for Hydrogen Storage: A Case Study with Alkali Metal Amidozincates


The alkali metal amidozincates Li[Zn(NH$_3$)$_2$]Ni(NH$_3$)$_2$ and K$_2$[Zn(NH$_3$)$_2$] were, to the best of our knowledge, studied for the first time as hydrogen storage media. Compared with the LiNH$_2$–2LiH system, both Li$_4$[Zn(NH$_3$)$_2$][NH$_3$]$_2$–12LiH and K$_2$[Zn(NH$_3$)$_2$]–8LiH systems showed improved rehydrogenation performance, especially K$_2$[Zn(NH$_3$)$_2$]–8LiH, which can be fully hydrogenated within 30 s at approximately 230 °C. The absorption properties are stable upon cycling. This work shows that ternary amides containing transition metals have great potential as hydrogen storage materials.

Hydrogen is a clean, renewable, efficient and environmentally friendly energy carrier, regarded as a potential candidate for replacing fossil fuels. To utilize H$_2$ for mobile applications, storage materials must exhibit high gravimetric and volumetric H$_2$ capacities and rapid rates of reversible de-/rehydrogenation at moderate temperatures and suitable pressures.[1] Amide–hydride systems have received a lot of attention as potential candidates for on-board applications due to their high gravimetric and volumetric H$_2$ capacities.[2] For example, the LiNH$_2$–2LiH system can store more than 10.0 wt% of H$_2$ reversibly (LiNH$_2$ + 2LiH → Li$_4$NH + LiH + H$_2$ = Li$_4$N + 2H$_2$). However, the LiNH$_2$–2LiH system cannot meet the required performance criteria for proton exchange membrane fuel cells (PEMFCs), owing to its high thermodynamic stability and slow dehydrogenation kinetics. According to Chen et al.[3] the plateau pressure of the first step of desorption for LiNH$_2$–2LiH is 1 bar at circa 285 °C. To utilize amide–hydride systems for practical applications, a considerable amount of work has been done to improve thermodynamic and kinetic behavior. Varieties of amide–hydride systems with different thermodynamic and kinetic properties (e.g., Ca–N–H,[4] Mg–N–H,[5] Li–Ca–N–H,[6] Li–Ca–N–H,[7] Li–Al–N–H,[8] Li–B–N–H[9]) have been developed and studied. For example, the substitution of LiNH$_2$ by Mg(NH$_3$)$_2$ or the replacement of 2LiH with MgH$_2$ in the LiNH$_2$–2LiH system led to the development of Mg(NH$_3$)$_2$–2LiH/2LiH–MgH$_2$ (2LiNH$_2$ + MgH$_2$ → Li$_4$Mg(NH$_3$)$_2$ + 2H$_2$ = Mg(NH$_3$)$_2$ + 2LiH).[10] This work shows that ternary amides containing transition metals might be an important step towards the development of novel H$_2$ storage systems with improved thermodynamic and kinetic properties.

In this work, the H$_2$ sorption properties of alkali metal amidozincates, as far as we know, were studied for the first time. The study draws attention to the great potential of ternary amides containing transition metals as H$_2$ storage material. In the presented case, the K$_2$[Zn(NH$_3$)$_2$]–8LiH system can be fully hydrogenated at circa 230 °C within 30 s. These excellent absorption properties are maintained upon cycling. Interestingly, when performing a rehydrogenation measurement at 222 °C, the dehydrogenated Li$_4$[Zn(NH$_3$)$_2$][NH$_3$]$_2$–12LiH and K$_2$[Zn(NH$_3$)$_2$]–8LiH mixtures were able to absorb roughly 2.0 and 1.5 wt% H$_2$, respectively, within 30 s. Under the same temperature and H$_2$ pressure conditions, almost no H$_2$ was absorbed by the dehydrogenated LiNH$_2$–2LiH.

The studied systems were prepared by ball milling Li$_4$[Zn(NH$_3$)$_2$][NH$_3$]$_2$, K$_2$[Zn(NH$_3$)$_2$], and LiNH$_2$ with LiH in a molar...
ratio of 1:12, 1:8, and 1:2, respectively. Thermogravimetric (TG) combined with differential thermal analysis (DTA) and mass spectrometry (MS), namely, TG–DTA–MS, was employed to investigate the thermal decomposition performances. A Siewerts-type apparatus (HERA, Quebec, Canada) was used to test the de-/rehydrogenation properties. The structural evolution of the crystalline phases was studied by powder X-ray diffraction (PXRD).

TG–DTA–MS was employed to investigate the thermal decomposition performance of Li,[Zn(NH)_4]_2(NH)_2, K,[Zn(NH)_4]_2 and LiNH_2 (Figure 1). Different from the reference material (i.e., LiH, K,NH, and KZnN being formed in the first step of the reaction of Li,[Zn(NH)_4]_2(NH)_2 decomposition, which can be described according to Reaction (1)). According to Figure 2b, Li,[Zn(NH)_4]_2(NH)_2–12 LiH starts to release H_2 at circa 100 °C, which is around 72 °C lower than the onset temperature (172 °C) of the reference LiNH_2–2LiH (with regard to the H_2 release signal). Except for the shift to lower temperatures of the dehydrogenation temperatures, the shapes of the H_2 signals of Li,[Zn(NH)_4]_2(NH)_2–12 LiH and LiNH_2–2LiH measured by means of MS are similar. This suggests that the reaction mechanism for the second step of the decomposition reaction of Li,[Zn(NH)_4]_2(NH)_2–12 LiH involves the interaction of LiNH_2 (which is formed during the first decomposition step) with LiH. The catalytic effects of Zn and LiZnN may be the reason for the apparent shift of the dehydrogenation temperature of Li,[Zn(NH)_4]_2(NH)_2–12 LiH to lower temperatures, as observed in the ZnCl_2–LiNH_yLiH system. Sometimes, the H_2 desorption behavior of an amide–hydride system, in an open system (e.g., TG), is different from that of a closed system (e.g., Siewerts apparatus). That is because H_2 desorption in amide–hydride systems involves two different mechanisms. One is a solid–solid reaction mechanism and the other is an ammonia-mediated mechanism. Dehydrogenation properties of

LiNH_2, Figure 1a and b clearly shows the multi-step nature of the thermal decomposition reactions of both Li,[Zn(NH)_4]_2(NH)_2 and K,[Zn(NH)_4]_2.[11,12] After heating the specimens to circa 500 °C, TG showed that K,[Zn(NH)_4]_2, Li,[Zn(NH)_4]_2(NH)_2, and LiNH_2 had lost 27.5, 31.7, and 37.2 wt% respectively. As reported earlier,[12] upon heating to 500 °C, Li,[Zn(NH)_4]_2(NH)_2 released 31.5 wt% NH_3 using the decomposition pathways shown in Reactions (1) and (2), which correlates well with the result presented here (31.7 wt%).

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\begin{align*}
\text{Li,[Zn(NH)_4]_2(NH)_2} & \rightarrow 3 \text{LiNH}_2 + \text{LiZnN} + 2 \text{NH}_3 \\
6 \text{LiNH}_2 & \rightarrow 3 \text{Li}_2\text{NH} + 3 \text{NH}_3
\end{align*}
\]

Figure 1c shows that the onset and maximum peak temperatures of Li,[Zn(NH)_4]_2(NH)_2 decomposition to ammonia are at approximately 260 and 300 °C, which are more than 60 °C lower than that of the pristine LiNH_2. However, K,[Zn(NH)_4]_2 decomposed to ammonia at a much higher temperature (circa 350 °C) and the reaction quickly reached a peak temperature at 360 °C. It should be pointed out that the sudden “jump” visible in the MS signals of Figure 1c is due to the low sensitivity of the used MS towards NH_3.

The hydrogen storage properties of Li,[Zn(NH)_4]_2(NH)_2–12 LiH, K,[Zn(NH)_4]_2–8 LiH, and LiNH_2–2LiH were studied using TG–MS and a Siewerts-type apparatus (Figure 2). Figure 2a shows material weight losses for both Li,[Zn(NH)_4]_2(NH)_2–12 LiH and LiNH_2–2LiH equal to 6.1 wt% after heating to 400 °C. However, the TG onset temperature for Li,[Zn(NH)_4]_2(NH)_2–12 LiH is below 100 °C, which is roughly 70 °C lower than that of the LiNH_2–2LiH sample. The TG onset temperatures of K,[Zn(NH)_4]_2–8 LiH and LiNH_2–2LiH are almost the same; however, K,[Zn(NH)_4]_2–8 LiH loses approximately 4.2 wt% when heated to 400 °C. The weight loss of K,[Zn(NH)_4]_2–8 LiH significantly increases when the sample is heated above 425 °C. To compare the effect of ball milling time on the investigated samples, TG–DTA curves of Li,[Zn(NH)_4]_2(NH)_2–12 LiH and K,[Zn(NH)_4]_2–8 LiH mixtures after grinding for 2 min using an agate mortar and pestle are shown in Figure S1 in the Supporting Information. The NH_3 and H_2 MS traces recorded during the TG of Li,[Zn(NH)_4]_2(NH)_2–12 LiH, K,[Zn(NH)_4]_2–8 LiH and LiNH_2–2 LiH are summarized in Figure 2b and c. Based on these analyses, it appears that the materials release mostly H_2 upon decomposition. For K,[Zn(NH)_4]_2–8 LiH and LiNH_2–2 LiH, the amount of released NH_3 is almost undetectable. This could be due to the fact that the formed NH_3 is immediately captured by LiH[13] or that H_2 is released as a consequence of the direct reaction of amidates with LiH.[14] For the Li,[Zn(NH)_4]_2(NH)_2–12 LiH sample, a small amount of NH_3 seems to be released at approximately 190 °C. In addition, the dehydrogenation performance of Li,[Zn(NH)_4]_2(NH)_2–12 LiH is similar to that of LiNH_2–2 LiH sample after circa 250 °C. This could be due to LiNH_2, NH_3, and LiZnN being formed in the first step of the reaction of Li,[Zn(NH)_4]_2(NH)_2 decomposition, which can be described according to Reaction (1). After heating the specimens to circa 500 °C, TG showed that K,[Zn(NH)_4]_2, Li,[Zn(NH)_4]_2(NH)_2, and LiNH_2 had lost 27.5, 31.7, and 37.2 wt% respectively. As reported earlier,[12] upon heating to 500 °C, Li,[Zn(NH)_4]_2(NH)_2 released 31.5 wt% NH_3 using the decomposition pathways shown in Reactions (1) and (2), which correlates well with the result presented here (31.7 wt%).
Li$_2$[Zn(NH$_3$)$_4$]([NH$_3$]$_2$)$_{12}$LiH, K$_2$[Zn(NH$_3$)$_4$]–8LiH, and LiNH$_4$–2LiH, and LiNH$_4$–2LiH are measured in a Sieverts type apparatus (HERA, Quebec, Canada) are summarized in Figure S2. Despite the fact that the dehydrogenation capacities measured in a closed system are slightly different to an open system, the onset temperatures and dehydrogenation shapes of the desorption curves shown in Figures S2 and 2a are similar. The lower H$_2$ contents measured for the investigated materials in a closed system could be due to the formation of a H$_2$ back-pressure that might slow down and/or hinder the further release of H$_2$ from the material. A detailed analysis of the thermodynamic properties of the alkali metal amidozincates and LiH mixtures will be given in a separate publication.

To investigate the hydrogenation behavior of the system outlined here, the desorbed Li$_2$[Zn(NH$_3$)$_4$]([NH$_3$]$_2$)$_{12}$LiH, K$_2$[Zn(NH$_3$)$_4$]–8LiH and LiNH$_4$–2LiH, were hydrogenated at 300 °C and 50 bar H$_2$; the results are summarized in Figure 2d. It is shown that the absorption behavior of both Li$_2$[Zn(NH$_3$)$_4$]([NH$_3$]$_2$)$_{12}$LiH and K$_2$[Zn(NH$_3$)$_4$]–8LiH are better than that of LiNH$_4$–2LiH. The hydrogenation onset temperatures of the three samples are roughly 190 °C; however, the absorption rates of Li$_2$[Zn(NH$_3$)$_4$]([NH$_3$]$_2$)$_{12}$LiH and K$_2$[Zn(NH$_3$)$_4$]–8LiH are higher than that of LiNH$_4$–2LiH. The amount of H$_2$ absorbed is 4.0 wt% for LiNH$_4$–2LiH, 4.3 wt% for Li$_2$[Zn(NH$_3$)$_4$]([NH$_3$]$_2$)$_{12}$LiH, and 3.1 wt% for K$_2$[Zn(NH$_3$)$_4$]–8LiH.

It should be noted that the plateau and further absorption shown for Li$_2$[Zn(NH$_3$)$_4$]([NH$_3$]$_2$)$_{12}$LiH at circa 280 °C is due to a nonlinear temperature change of the furnace (shown in Figure S3). Interestingly, a sharp increase in the amount of H$_2$ absorbed in the K$_2$[Zn(NH$_3$)$_4$]–8LiH system occurs at about 230 °C. This implies an extremely fast hydrogenation rate for the K$_2$[Zn(NH$_3$)$_4$]–8LiH sample in the dehydrogenated state. The inset in Figure 2d shows that most of the absorbed H$_2$ (i.e., 2.5 wt%) is charged within 30 s for the K$_2$[Zn(NH$_3$)$_4$]–8LiH system. To the best of our knowledge, the hydrogenation rate shown by the desorbed K$_2$[Zn(NH$_3$)$_4$]–8LiH is the fastest reported in literature for amide–hydride systems.

Isothermal de-/rehydrogenation experiments were employed to investigate the H$_2$ properties of the studied systems. Figures S4 and 3 summarize the H$_2$ properties of these materials for the dehydrogenation process measured at 192 °C and the rehydrogenation process at 222 °C. After 7 h, the amount of H$_2$ released by the materials were 2.4, 2.3, and 1.4 wt% for LiNH$_4$–2LiH, Li$_2$[Zn(NH$_3$)$_4$]([NH$_3$]$_2$)$_{12}$LiH, and K$_2$[Zn(NH$_3$)$_4$]–8LiH, respectively (Figure S4). The sorption kinetics of Li$_2$[Zn(NH$_3$)$_4$]([NH$_3$]$_2$)$_{12}$LiH and K$_2$[Zn(NH$_3$)$_4$]–8LiH are remarkably faster compared to that of the reference LiNH$_4$–2LiH system. The inset in Figure 3 shows that both Li$_2$[Zn(NH$_3$)$_4$]([NH$_3$]$_2$)$_{12}$LiH and
K\textsubscript{2}[Zn(NH\textsubscript{2})\textsubscript{4}]-8LiH can be charged within 30 s. However, in the same range of time almost no H\textsubscript{2} was absorbed by the LiNH\textsubscript{2}-2LiH system.

Temperature-programmed volumetric desorption and subsequent absorption measurements on the K\textsubscript{2}[Zn(NH\textsubscript{2})\textsubscript{4}]-8LiH sample were performed for three cycles to investigate the reversibility (Figure 4). The results indicate that roughly 3 wt% H\textsubscript{2} can be reversibly desorbed and absorbed in K\textsubscript{2}[Zn(NH\textsubscript{2})\textsubscript{4}]-8LiH. It is interesting that the quick “absorption jump” at about 230 °C was present in all the absorption tests. In addition, de-/rehydrogenation properties of the third cycle are better than that of the second one, which could be due to phase segregation and not perfect intermixing of the reactants.

To shed some light on the reaction mechanism of the de-/rehydrogenation of Li\textsubscript{2}[Zn(NH\textsubscript{2})\textsubscript{4}]-12LiH and K\textsubscript{2}[Zn(NH\textsubscript{2})\textsubscript{4}]-8LiH, de-/absorption products were investigated by PXRD and compared to the LiNH\textsubscript{2}-2LiH system. The results of this investigation are summarized in Figure 5 together with the PXRD patterns of the as-milled Li\textsubscript{2}[Zn(NH\textsubscript{2})\textsubscript{4}](NH\textsubscript{3})\textsubscript{2}-12LiH, K\textsubscript{2}[Zn(NH\textsubscript{2})\textsubscript{4}]-8LiH, and LiNH\textsubscript{2}-2LiH. The structural changes of the LiNH\textsubscript{2}-2LiH system are the same as reported previously\textsuperscript{[2a]} Upon dehydrogenation, LiNH\textsubscript{2}-2LiH converts into Li\textsubscript{2}NH and LiH, which after hydrogenation, changes back to LiNH\textsubscript{2}-2LiH (Figure 5a). Only LiNH\textsubscript{2} and LiH appear in the post-ball-milled Li\textsubscript{2}[Zn(NH\textsubscript{2})\textsubscript{4}](NH\textsubscript{3})\textsubscript{2}-12LiH sample (Figure 5b; Zn appeared to be PXRD amorphous as shown in Figure S5), which indicates that the first step of the decomposition reaction of Li\textsubscript{2}[Zn(NH\textsubscript{2})\textsubscript{4}](NH\textsubscript{3})\textsubscript{2} could occur during ball milling. After treating the Li\textsubscript{2}[Zn(NH\textsubscript{2})\textsubscript{4}](NH\textsubscript{3})\textsubscript{2}-12LiH mixture at 350 °C, Li\textsubscript{2}NH and LiZn\textsubscript{13} formed. The materials rehydrogenated at 300 °C and 90 bar H\textsubscript{2}, showing the conversion of Li\textsubscript{2}NH into LiNH\textsubscript{2} and LiH; however, LiZn\textsubscript{13} is still present. This suggests that the desorp-
possible reasons for the fast rehydrogenation kinetics of K$_2$[Zn(NH$_2$)$_3$]$_3$–8LiH could be as follows: 1) Changes in sample morphology of K$_2$[Zn(NH$_2$)$_3$]$_3$–8LiH before and after dehydrogenation indicate the sample could have been in a molten state at circa 230 °C (Figure S6). This molten state could aid in mass transportation during the hydrogenation process due to the Zn$^{2+}$ sites becoming more readily available, increasing the likelihood of H$_2$ dissociation, which will accelerate the rate of hydrogenation. 2) An unknown compound was observed during the desorption and absorption processes (Figure S5), this unknown compound could act as a “catalyst” during desorption, thereby increasing the reaction kinetics. A detailed investigation of de-/rehydrogenation mechanisms and reversibility of Li$_2$[Zn(NH$_2$)$_3$]$_3$[NH$_4$]$_2$–12LiH and K$_2$[Zn(NH$_2$)$_3$]$_3$–8LiH samples are currently underway and will be reported in a future work.

In summary, ternary amides containing alkali and transition metals were studied for the first time as H$_2$ storage materials. After mixing Li$_2$[Zn(NH$_2$)$_3$]$_3$[NH$_4$]$_2$ and K$_2$[Zn(NH$_2$)$_3$]$_3$ with LiH, they released 6.1 and 4.2 wt % H$_2$ below 400 °C, respectively. Compared to the reference LiNH$_2$–2LiH, both Li$_2$[Zn(NH$_2$)$_3$]$_3$[NH$_4$]$_2$–12LiH and K$_2$[Zn(NH$_2$)$_3$]$_3$–8LiH showed improved rehydrogenation performance. Moreover, the desorbed K$_2$[Zn(NH$_2$)$_3$]$_3$–8LiH sample can be hydrogenated within 30 s at 230 °C and 50 bar H$_2$ with a maximum rehydrogenation rate of approximately 6.0 wt % min$^{-1}$; this is, to the best of our knowledge, the fastest rehydrogenation rate observed to date in amide–hydride systems. In addition, the extremely good absorption properties of K$_2$[Zn(NH$_2$)$_3$]$_3$–8LiH are stable upon cycling. It should be pointed out that the gravimetric and volumetric H$_2$ capacities and operating temperature of alkali metal amidozincates still do not meet the targets for on-board vehicular application; however, the large variety of ternary amides that can be prepared opens new perspectives for the development of an amide-based H$_2$ storage material for mobile applications.

**Experimental Section**

LiNH$_2$ (95% purity) and LiH (97% purity) were purchased from Strem and Alfa, respectively. Li$_2$[Zn(NH$_2$)$_3$]$_3$[NH$_4$]$_2$ and K$_2$[Zn(NH$_2$)$_3$]$_3$ were synthesized in supercritical ammonia in custom-built Alloy 718 (austenitic Ni–Cr-based superalloy) autoclaves. Li$_2$[Zn(NH$_2$)$_3$]$_3$[NH$_4$]$_2$ was grown in the cold temperature zone of the autoclave under ammonothermal conditions (500 °C furnace temperature and 110 MPa NH$_3$) from Zn, Li (molar metal ratio 1:4) and supercritical ammonia. K$_2$[Zn(NH$_2$)$_3$]$_3$ was obtained in the cold temperature zone of the autoclave from Zn powder and K amide (molar metal ratio 1:2) under ammonothermal conditions (300 °C furnace temperature, 150 MPa NH$_3$). Powder X-ray diffraction analyses (PXRD) of the as-synthesized Li$_2$[Zn(NH$_2$)$_3$]$_3$[NH$_4$]$_2$ and Li$_2$[Zn(NH$_2$)$_3$]$_3$ and the commercial LiNH$_2$ are summarized in Figure S7. LiNH$_2$–2LiH, Li$_2$[Zn(NH$_2$)$_3$]$_3$[NH$_4$]$_2$–12LiH, and K$_2$[Zn(NH$_2$)$_3$]$_3$–8LiH samples were ball milled for 12 h at 250 rpm using a Fritsch Pulverisette 6 (Germany) classic line planetary mill, with a ball-to-powder ratio of circa 40:1 in a high-pressure vial with 50 bar H$_2$. All powder handling and milling were performed in an MBrán (Germany) Ar glovebox with H$_2$O and O$_2$ levels below δ = 10 ppm to prevent contamination. Thermogravimetric analysis (TG), differential thermal analysis (DTA) as well as mass spectrometry (MS) measurements were carried out using a Netzsch STA 409 C (Germany) and a Hiden Analytical HAL 201 Mass-Spectrometer (United Kingdom) combined system in 50 ml min$^{-1}$ Ar flow. The samples were investigated in the range of 20–500 °C using a heating rate of 5 °C min$^{-1}$. In addition, the gases had to flow through a capillary (circa 2 m) connecting the TG with the MS before reaching the MS.

De-/rehydrogenation experiments were performed using a Sieverts-type apparatus (HERA, Quebec, Canada). Absorption was heated up to the final temperature of 300 °C under a H$_2$ pressure of 50 bar using a heating rate of 3 °C min$^{-1}$. Desorption experiments were performed from room temperature to 400 °C under vacuum at a heating rate of 3 °C min$^{-1}$. Isothermal de-/rehydrogenation experiments were performed using a Sieverts-type apparatus (HERA, Quebec, Canada) at a temperature of 192 and 222 °C and vacuum and 50 bar H$_2$, respectively. PXRD tests were carried out using a Bruker D8 discover X-ray diffractometer (Germany) with Cu radiation (λ = 0.154 nm, 50 kV, 1000 μA) at a scanning rate of 0.05 degrees$^{-1}$. Air-tight sample holders were used (Bruker, Germany) to prevent contamination of the sample. All de-/rehydrogenated samples were heated to 350 °C in vacuum and 300 °C under 90 bar H$_2$ overnight before the PXRD test.

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