Mechanochemical synthesis and effect of various additives on the hydrogen absorption–desorption behavior of Na_3AlH_6

Kateryna Peinecke¹, Mariem Meggouh¹, and Michael Felderhoff^{1,*}

¹ Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

Received: 15 February 2018

Accepted: 28 March 2018

Published online:
9 April 2018

© The Author(s) 2018

ABSTRACT

Sodium aluminum hydride has been extensively investigated for hydrogen storage applications whereas its intermediate decomposition compound Na_3AlH_6 received much less attention, despite having a lower dissociation pressure and a reasonable hydrogen storage capacity of 3.0 wt%. In this work, Na_3AlH_6 is synthesized through ball milling, starting from NaAlH_4 and 2 NaH in the presence of TiCl_3 catalyst precursor, and evaluated on its hydrogen sorption properties and cycle stability. Further addition of 8 mol% Al and 8 mol% activated carbon (AC) and their effect on both the hydrogen sorption properties and cycle stability have been investigated. In order to explore whether the introduction of the Al and AC additives would be more beneficial (in terms of hydrogen sorption behavior and cycle stability) after the Na_3AlH_6 synthesis or during its synthesis, pre-synthesized Na_3AlH_6 -based measurements were also included in this work. TiCl_3 -catalyzed $\text{NaAlH}_4 + 2 \text{NaH}$ sample showed a stable reversible hydrogen storage capacity of 1.7 wt%, which was further increased to 2.1 wt% with the addition of Al-powder and activated carbon AC.

Introduction

Complex metal hydrides have gained much interest as hydrogen storage materials for practical applications due to their relative high theoretical gravimetric hydrogen capacity. Unfortunately, many complex metal hydrides require high pressures and temperatures for their hydrogenation and high temperature for dehydrogenation. Researchers have therefore focused on altering the thermodynamics for dehy-

drogenation of these complex metal hydrides to lower the temperature of hydrogen release and improving the kinetics for the hydrogenation and dehydrogenation reactions [1, 2]. Among the complex metal hydrides, sodium alanate, NaAlH_4 , has acquired much attention as a potential hydrogen storage material since it was reported to be reversible through doping with small amounts of Ti-catalysts [3]. NaAlH_4 has a theoretical reversible hydrogen

Address correspondence to E-mail: felderhoff@mpi-muelheim.mpg.de

storage capacity of 5.6 wt% and releases its hydrogen according to Eqs. (1) and (2).

Despite its lower hydrogen capacity of 3.0 wt%, Na_3AlH_6 has attracted also attention as a potential hydrogen storage material, because of much lower dissociation pressure than NaAlH_4 (6 vs. 66 bar at 150 °C, respectively) and therefore making it more suitable for practical applications [3]. Formed in the first decomposition step of NaAlH_4 (1), Na_3AlH_6 can also be directly synthesized through the reaction of 2 NaH and NaAlH_4 in heptane at 160 °C [4] or through hydrogenation of Na and Al in toluene at 165 °C [5]. More recently, direct synthesis of $\beta\text{-Na}_3\text{AlH}_6$ was also achieved through mechanical milling of NaAlH_4 and 2 NaH [6] and from NaH and Al in the presence of 4 mol% TiF_3 under hydrogen pressure [7]. Furthermore, it was found that Na_3AlH_6 synthesized through mechanical milling exhibited faster kinetics than Na_3AlH_6 obtained from the decomposition of NaAlH_4 [8]. Na_3AlH_6 proved to be reversible through the addition of Ti compounds [3]; however, doping with Zr compounds was reported to have better effect on the dehydrogenation of Na_3AlH_6 than doping with Ti [8, 9]. Although a large number of experimental results have been described on NaAlH_4 , a small number of studies have been reported on Na_3AlH_6 and its use as a hydrogen storage material. So far the studies on Na_3AlH_6 deal with theoretical calculations of structural parameters, effect of Ti doping, and hydrogen diffusion in pure and Ti-doped Na_3AlH_6 . To our knowledge, no extensive study on the direct synthesis of Na_3AlH_6 through mechanochemical processes and the effect of various additives on the hydrogenation and dehydrogenation behavior has been reported so far. In this work, we investigate the synthesis of Na_3AlH_6 starting from NaAlH_4 and NaH in the presence of TiCl_3 , combined with the addition of Al and AC. It has been reported that addition of AC to Ti-doped NaAlH_4 not only resulted in improved dehydrogenation and hydrogenation kinetics but also enhanced the cycle life [10] and ability to conduct heat [11]. We also investigate whether the additives are best added during or after the Na_3AlH_6 synthesis in order to obtain the optimum performance of the material. The long-term cycle stability measurements are performed at 170 °C, which allows using this material in combination with HT-PEM fuel cells.

Experimental

The starting materials NaH (60% dispersion in mineral oil, Sigma-Aldrich Chemical) and NaAlH_4 (technical grade, Sigma-Aldrich Chemical) were further purified to obtain 98% purity. NaH was cleaned from mineral oil by washing with pentane and NaAlH_4 was purified by dissolving in THF solution, and then recrystallized using toluene. TiCl_3 (ReagentPlus®, Sigma-Aldrich Chemical), AC (activated carbon) ($0.79 \text{ cm}^3 \text{ g}^{-1}$, Carbo Tech), Al (99%, Aluminum Rheinfelden), and doped NaAlH_4 with 4 mol% TiCl_3 (prepared in house) were used without further purification. The samples (2.2 g) were prepared by mechanical milling for 4 h under inert atmosphere (Ar) using hardened steel grinding bowls and grinding balls ($\phi = 10 \text{ mm}$) in a Fritsch Planetary Mono Mill Pulverisette 6 at 450 rpm, with a ball-to-powder ratio of 30:1.

The samples characterized by X-ray diffraction were measured in transmission mode with a curved germanium (111) monochromator (STOE STADI P). Five samples: as-received NaH, as-received NaAlH_4 , as-milled $\text{NaAlH}_4 + 4 \text{ mol\% TiCl}_3$, $\text{NaAlH}_4 + 4 \text{ mol\% TiCl}_3 + 2 \text{ NaH}$, and $\text{NaAlH}_4 + 4 \text{ mol\% TiCl}_3 + 2 \text{ NaH} + 8 \text{ mol\% Al} + 8 \text{ mol\% AC}$ were characterized using an image plate detector, Cu-K α radiation ($1.541 \text{ \AA}$), and capillary ($\phi = 0.5 \text{ mm}$). Three as-milled samples: Na_3AlH_6 , $\text{Na}_3\text{AlH}_6 + 4 \text{ mol\% TiCl}_3$, and $\text{Na}_3\text{AlH}_6 + 4 \text{ mol\% TiCl}_3 + 8 \text{ mol\% Al} + 8 \text{ mol\% AC}$ were characterized using a Mythen1K detector, Mo-radiation ($0.7093 \text{ \AA}$), and capillary ($\phi = 0.5 \text{ mm}$).

Differential scanning calorimetry (DSC) measurements were carried out with a Mettler-Toledo TGA/DSC1 Star^e System, under 1 bar of flowing argon (50 ml min^{-1}) with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from room temperature to a maximum temperature of 450 °C. Thermal gravimetric analysis (TGA) measurements were carried out with a NETZSCH STA 449 C Jupiter, under 1 bar of flowing argon (50 ml min^{-1}) with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ (Na_3AlH_6 -based samples) or $2 \text{ }^\circ\text{C min}^{-1}$ (NaAlH_4 -based samples) from room temperature to a maximum temperature of 450 °C. Handling and storing of samples were performed in an inert atmosphere (Ar) glove box (MBraun Unistar) with $< 1 \text{ ppm O}_2$ and $< 1 \text{ ppm H}_2\text{O}$.

Absorption–desorption cycle measurements were performed on a PCT-Pro 2000 (SETARAM). The tests

were carried out using 2 g of material which was placed in the sample holder using an argon-filled glove box. Several stainless steel spacers were used to center the sample inside the sample holder, thereby reducing the empty space of the sample holder and increasing the accuracy of the measurement. The pressure was monitored using an MKS pressure transducer with an accuracy of 1.0% of the reading value. The temperature of the sample was measured inside the sample holder well using a type K thermocouple with an accuracy of ± 1.1 °C. The mass of the samples was measured on SCALTEC SBA 42 balance with an accuracy of ± 0.003 g. The cycling conditions were performed at 170 °C, with 2-h hydrogenation cycles at 25 bar hydrogen pressure and 2-h dehydrogenation cycles at 0.1 bar hydrogen pressure.

Results and discussion

Ball-milled samples

Figure 1 shows the X-ray diffraction (XRD) patterns of the starting materials NaH (Fig. 1a) and NaAlH₄ (Fig. 1b) together with as-milled NaAlH₄ containing samples. It was observed that ball milling (4 h) of NaAlH₄ in the presence of 4 mol% TiCl₃ resulted in the partial decomposition of NaAlH₄ as diffraction peaks of Na₃AlH₆, NaCl, and Al were found (Fig. 1c).

Figure 1 XRD diffraction patterns for: *a* as-received NaH, *b* as-received NaAlH₄, *c* as-milled NaAlH₄ + 4 mol% TiCl₃, *d* as-milled NaAlH₄ + 2 NaH + 4 mol% TiCl₃, and *e* as-milled NaAlH₄ + 2 NaH + 4 mol% TiCl₃ + 8 mol% Al + 8 mol% AC (Cu-K α radiation, 1.541 Å).

Synthesis of Na₃AlH₆ was best achieved through ball milling of 2 mol of NaH and NaAlH₄, in the presence of 8 mol% of Al and AC (Fig. 1e) which showed (in contrary to Fig. 1d) no diffraction peaks of remaining NaH. Although TiCl₃ has been successfully applied as a dopant for sodium alanate systems, the catalytic mechanism remains unclear. It has been reported that during ball milling the titanium of TiCl₃ is reduced to its metallic state [12]. However, addition of metallic titanium to NaAlH₄ resulted in lower dehydrogenation capacities, indicating that the reduction in the dopant plays more complex role than presumed. The same applies for the Al–Ti compounds that have been proposed as the active species (rather than Ti), but when directly added, the similar results as for non-doped samples were obtained. Bogdanović et al. and Singh et al. reported that although the formation of NaCl as a by-product reduces the overall reversible hydrogen capacity, it acts as a grain refiner for NaH. Similarly, Al_xTi_y species have been found to act as a grain refiner for Al as well, preventing particle growth [12–14]. The presence of grain refiners in combination with the vacancies and defects created during the ball-milling process seems to be crucial. It improves the mass transfer during hydrogenation and dehydrogenation, allowing faster kinetics. The absence of grain refiners would explain the poor results obtained for systems in which metallic Ti or Al–Ti was directly added [14].

In order to investigate the doping effect of the various additives, pre-synthesized Na₃AlH₆ was used (Fig. 2). XRD measurements showed that addition of 4 mol% TiCl₃ alone did not result in a significant decomposition of Na₃AlH₆ (Fig. 2b), the weak NaAlH₄ diffraction peak at 2θ values of 22° was already present in the pre-synthesized Na₃AlH₆ (Fig. 2a). Furthermore, addition of 8 mol% of both Al and AC showed no appearance of new phases (Fig. 2c). In fact, samples (b) and (c) are very similar.

Sandrock et al. [15] reported that although TiCl₃ enhances the dehydriding and hydriding kinetics for both NaAlH₄ and Na₃AlH₆, the effect is more pronounced for NaAlH₄ than for Na₃AlH₆ (activation energy (desorption) for non-catalyzed NaAlH₄ = 118 kJ mol^{−1} (H₂), catalyzed (4 mol% TiCl₃) NaAlH₄ = 80 kJ mol^{−1} (H₂), non-catalyzed Na₃AlH₆ = 121 kJ mol^{−1} (H₂), catalyzed (4 mol% TiCl₃) Na₃AlH₆ = 98 kJ mol^{−1} (H₂)). From the obtained XRD data, it seems that Na₃AlH₆ is less reactive toward the TiCl₃ catalyst than NaAlH₄, as no partial

Figure 2 XRD diffraction patterns for *a* as-prepared Na_3AlH_6 , *b* as-milled Na_3AlH_6 + 4 mol% TiCl_3 , and *c* as-milled Na_3AlH_6 + 4 mol% TiCl_3 + 8 mol% Al + 8 mol% AC (Mo-radiation, 0.7093 Å).

decomposition of Na_3AlH_6 was observed (i.e., formation of NaCl and NaH). This was further emphasized by in situ pressure recording measurements during ball milling (Fig. 3) which showed that the pressure (from released hydrogen during the reduction of TiCl_3) inside the milling vial increased to 5.2 bar for catalyzed NaAlH_4 , but only to 0.7 bar for catalyzed Na_3AlH_6 . These results allowed for rough estimation of the molar quantity of NaCl produced assuming all TiCl_3 has reacted, giving overall Eq. (3) and reversible

Figure 3 Pressure increase (from released hydrogen) during ball-milling process, *a* NaAlH_4 + 4 mol% TiCl_3 , *b* milled Na_3AlH_6 + 4 mol% TiCl_3 . Note The hydrogen release zero value starts at 1 bar.

hydrogen storage of 2.46 wt% for NaAlH_4 + 2 NaH + 4 mol% TiCl_3 as shown in Eq. (4). For the additive containing sample, the Al addition results in a slightly higher reversible hydrogen capacity (2.61 wt%), see Eqs. (5) and (6).

Thermal dehydrogenation

Thermal decomposition behavior of the NaAlH_4 -based samples was investigated using DSC measurements. Figure 4 shows the DSC curves of as-received starting materials NaH (Fig. 4a) and NaAlH_4 (Fig. 4b) together with milled samples when heated from room temperature to 450 °C under 1 bar of flowing argon at a heating rate of 10 °C min⁻¹. NaAlH_4 in the presence of the TiCl_3 catalyst precursor (Fig. 4c) showed small and weak endothermic events at 139 and 396 °C, corresponding to the

Figure 4 DSC curves for *a* as-received NaH , *b* as-received NaAlH_4 , *c* milled NaAlH_4 + 4 mol% TiCl_3 , *d* milled NaAlH_4 + 2 NaH + 4 mol% TiCl_3 , and *e* milled NaAlH_4 + 2 NaH + 4 mol% TiCl_3 + 8 mol% Al + 8 mol% AC . Samples were heated to 450 °C under 1 bar of flowing argon at 10 °C min⁻¹. *, melting of NaAlH_4 ; •, decomposition of NaAlH_4 ; ▲, decomposition of Na_3AlH_6 ; Δ, decomposition of NaH .

decomposition of NaAlH_4 and NaH which both occurred at much lower temperatures than their respective as-received materials, demonstrating the kinetic effect of the catalyst precursor. The weak and broad endothermic event between 169 and 227 °C is contributed to the decomposition of Na_3AlH_6 (supported by TGA data, Fig. 7), whereas the cause for the exothermic event at 243 °C remains unclear. The most pronounced effect was observed for the sample containing ball-milled NaAlH_4 in the presence of 2 mol of NaH and 4 mol% TiCl_3 (Fig. 4d), which showed a double endothermic peak for the decomposition of Na_3AlH_6 between 225 and 250 °C, followed by the endothermic peak for the decomposition of NaH around 390 °C. No endothermic events corresponding to NaAlH_4 were observed, further supporting the full conversion of NaAlH_4 into Na_3AlH_6 during the ball-milling process as observed from XRD data (Fig. 1d). Further addition of Al and AC (Fig. 4e) resulted in a similar curve as obtained for the TiCl_3 -doped sample (Fig. 4c).

Figure 5 shows the DSC measurements for the Na_3AlH_6 containing milled samples which displayed no significant change for the thermal events, as found for the NaAlH_4 containing samples, when heated from room temperature to 450 °C under 1 bar of flowing argon at a heating rate of 10 °C min^{-1} . As-received Na_3AlH_6 showed two main endothermic events, the first is a complex event between 243 and

304 °C, corresponding to the decomposition of Na_3AlH_6 into elemental Al and NaH . The second endothermic signal which occurred at 385 °C was caused by the decomposition of NaH . For the TiCl_3 -catalyzed Na_3AlH_6 sample (Fig. 5b), the endothermic signal for the Na_3AlH_6 decomposition step was observed at much lower temperatures (185–278 °C), whereas the endothermic peak for the decomposition of NaH took place at a higher temperature (391 °C). However, the lowest peak temperatures were obtained for the catalyzed Na_3AlH_6 sample with additional 8 mol% of Al and AC (Fig. 5c) with the Na_3AlH_6 decomposition reaction between 177 and 265 °C and the NaH decomposition peak at 370 °C.

Na_3AlH_6 is known to undergo phase transformation of $\alpha\text{-Na}_3\text{AlH}_6$ to $\beta\text{-Na}_3\text{AlH}_6$ around 252 °C [15, 16], and in order to detect this phase transformation rapid heating and fast data acquisition is needed [17]. Weidenthaler et al. [18] investigated the phase transformation using in situ DSC and high-temperature X-ray diffraction methods and found that using different heating rate resulted in different decomposition behavior. For example, they observed that the endothermic signals for the decomposition of Na_3AlH_6 and NaH shifted to higher temperatures with higher heating rates. A shoulder (~ 248 °C) at the Na_3AlH_6 decomposition signal became apparent at heating rates $> 10 \text{ K min}^{-1}$, suggesting that another reaction is taken place prior to the decomposition of Na_3AlH_6 [18]. Figure 5a shows a shoulder

Figure 5 DSC curves for *a* as-received Na_3AlH_6 , *b* Na_3AlH_6 + 4 mol% TiCl_3 , and *c* Na_3AlH_6 + 4 mol% TiCl_3 + 8 mol% Al + 8 mol% AC . Samples were heated to 450 °C under 1 bar of flowing argon at 10 °C min^{-1} ; $\blacktriangle$, decomposition of Na_3AlH_6 ; and Δ , decomposition of NaH .

Figure 6 TGA curves for *a* as-received NaAlH_4 , *b* milled NaAlH_4 + 4 mol% TiCl_3 , *c* milled NaAlH_4 + 2 NaH + 4 mol% TiCl_3 , and *d* milled NaAlH_4 + 2 NaH + 4 mol% TiCl_3 + 8 mol% Al + 8 mol% AC . Samples were heated to 300 °C under 1 bar of flowing argon at 2 °C min^{-1} .

at 256 °C which is believed to be the phase transformation of α - Na_3AlH_6 to β - Na_3AlH_6 . However, in the doped samples (Fig. 5b, c) this shoulder is not observed and is most likely due to increased kinetics resulting in the decomposition of α - Na_3AlH_6 to NaH and Al without detectable formation of β - Na_3AlH_6 .

The dehydrogenation curves for the NaAlH_4 - and Na_3AlH_6 -based samples are shown in Figs. 6 and 7, respectively, with their corresponding hydrogen release capacities listed in Table 1. As-received NaAlH_4 (Fig. 6a) showed an onset dehydrogenation temperature of 189 °C and hydrogen release capacity of 5.5 wt%, which is close to its theoretical capacity of 5.6 wt%. However, addition of 4 mol% of TiCl_3

Figure 7 TGA curves for *a* as-received Na_3AlH_6 , *b* Na_3AlH_6 + 4 mol% TiCl_3 , and *c* Na_3AlH_6 + 4 mol% TiCl_3 + 8 mol% Al + 8 mol% AC. Samples were heated to 300 °C under 1 bar of flowing argon at 10 °C min⁻¹.

(Fig. 6b) resulted in an onset dehydrogenation temperature of 90 °C, a shift of roughly 100 °C compared to the pristine material, releasing hydrogen capacity of 4.2 wt%. For Na_3AlH_6 , the effect of TiCl_3 was less pronounced (Fig. 7b) and resulted in a shift of roughly 50 °C to lower temperatures and hydrogen release capacity of 2.3 wt% compared to 2.4 wt% for the pristine Na_3AlH_6 (Table 1). From XRD data (Fig. 2b), this small effect was expected as no change was observed compared to pristine Na_3AlH_6 .

For the sample containing both 4 mol% TiCl_3 and 2 mol NaH (Fig. 6c), the onset dehydrogenation temperature shifted to higher temperatures in comparison with the sample containing 4 mol% TiCl_3 (Fig. 6b) and the sample containing 4 mol% TiCl_3 , 2 mol NaH, 8 mol% Al, and 8 mol% AC (Fig. 6d) and occurred at 206 °C, providing a hydrogen release capacity of 2.0 wt% (Table 1). From XRD data (Fig. 1d), it could be observed that Na_3AlH_6 which was synthesized in situ through the addition of NaH resulted in a lower onset dehydrogenation temperature than found for as-received Na_3AlH_6 (233 °C), Fig. 7a. In Fig. 6d, it can be seen that the hydrogen release capacity increased to 2.5 wt% (Table 1) when 8 mol% of Al and AC were added to the NaAlH_4 + 2 NaH + 4 mol% TiCl_3 sample and gave an onset dehydrogenation temperature of 149 °C. Similar results were obtained for the doped Na_3AlH_6 sample when 8 mol% of both Al and AC were added, showing an onset dehydrogenation temperature of 171 °C and a hydrogen release capacity of 2.6 wt%. It seems that, for both the NaAlH_4 - and Na_3AlH_6 -based samples, the Al and AC additives reduced the onset

Table 1 Theoretical and experimental hydrogen capacities for the NaAlH_4 - and Na_3AlH_6 -based samples

Sample	Theoretical hydrogen capacity (wt%)	Hydrogen capacity according to Eqs. (4) and (6) (wt%)	Experimental hydrogen capacity (wt%)
NaAlH_4 as-received	5.6	5.6	5.5
NaAlH_4 + 4 mol% TiCl_3	5.2	4.4	4.2
NaAlH_4 + 2 NaH + 4 mol% TiCl_3	2.9	2.5	2.0
NaAlH_4 + 2 NaH + 4 mol% TiCl_3 + 8 mol% Al + 8 mol% AC	2.8	2.6	2.5
Na_3AlH_6 as-received	3.0	3.0	2.4
Na_3AlH_6 + 4 mol% TiCl_3	2.9	2.5	2.3
Na_3AlH_6 + 4 mol% TiCl_3 + 8 mol% Al + 8 mol% AC	2.8	2.6	2.6

Figure 8 Long-term cycle stability test of milled $\text{Na}_3\text{AlH}_6 + 4 \text{ mol\% TiCl}_3$ after 750 h of operation with 2 h cycles of hydrogenation (28 bar H_2) and dehydrogenation (0.1 bar H_2) at 170 °C.

Figure 9 Long-term cycle stability test of milled $\text{Na}_3\text{AlH}_6 + 4 \text{ mol\% TiCl}_3 + 8 \text{ mol\% Al} + 8 \text{ mol\% AC}$ after 750 h of operation with 2-h cycles of hydrogenation (28 bar H_2) and dehydrogenation (0.1 bar H_2) at 170 °C.

dehydrogenation temperatures further, possibly by increasing the dehydrogenation kinetics and the increased hydrogen release capacity through addition of Al as proposed in Eqs. (5) and (6).

Cycle stability measurements

Figure 8 shows the cycle stability measurement for the $\text{Na}_3\text{AlH}_6 + 4 \text{ mol\% TiCl}_3$ sample when subjected to 2-h hydrogenation (28 bar H_2)/dehydrogenation (0.1 bar H_2) cycles at 170 °C. The sample showed good cycle stability with a hydrogen capacity of 1.6 wt% at the start of the measurement which increased slightly to 1.7 wt% after 750 h [19]. No capacity loss was observed till 650 h of operation. However, at 650 h the capacity loss of $\sim 10\text{--}15\%$ which lasted only for a few cycles (Fig. 8) was observed. This capacity loss was not observed for the $\text{Na}_3\text{AlH}_6 + 4 \text{ mol\% TiCl}_3 + 8 \text{ mol\% Al} + 8 \text{ mol\% AC}$ sample and it's unclear as to the reason for its occurrence.

Addition of 8 mol% Al and 8 mol% AC to the Na_3AlH_6 with 4 mol% TiCl_3 (same cycling conditions as for the $\text{Na}_3\text{AlH}_6 + 4 \text{ mol\% TiCl}_3$ sample) resulted in an increased hydrogen capacity of 2.2 wt% (Fig. 9) in comparison with 1.7 wt% (Fig. 8). The sample showed good cycle stability and in contrary to the $\text{Na}_3\text{AlH}_6 + 4 \text{ mol\% TiCl}_3$ sample, no capacity losses were observed during 750 h of operating. Electricity shutdown caused some interruption at around 50, 170, 250, and 480 h since beginning of the experiment.

Conclusions

Ball-milled sample containing $\text{NaAlH}_4 + 2 \text{ NaH} + 4 \text{ mol\% TiCl}_3 + 8 \text{ mol\% Al} + 8 \text{ mol\% AC}$ gave better results compared to the sample containing $\text{NaAlH}_4 + 2 \text{ NaH} + 4 \text{ mol\% TiCl}_3$, with hydrogen capacities of 2.2 and 1.7 wt%, respectively. The addition of Al allowed for the remaining NaH to react further into Na_3AlH_6 during the hydrogenation process, thereby increasing the hydrogen capacity. Cycle life stability measurements for both samples showed no sign of performance loss up to 750 h of operation, allowing the use as hydrogen storage materials in combination with HT-PEM fuel cell applications.

Acknowledgements

Open access funding provided by Max Planck Society. Financial support by Ministerium für Wirtschaft, Energie, Bauen, Wohnen und Verkehr des Landes Nordrhein-Westfalen and European Regional Development Fund (ERDF) (Funding No. ef003a) is much appreciated. The authors gratefully acknowledge the Max Planck Society for basic funding. The authors thank Dr. Claudia Weidenthaler and Jan Ternieden for measurement and interpretation of X-ray diffraction patterns.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- [1] Jain IP, Jain P, Jain A (2010) Novel hydrogen storage materials: a review of lightweight complex hydrides. *J Alloys Compd* 503:303–339
- [2] Sakintuna B, Lamari-Darkrim F, Hirscher M (2007) Metal hydride materials for solid hydrogen storage: a review. *Int J Hydrogen Energy* 32:1121–1140
- [3] Bogdanović B, Schwickardi M (1997) Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials. *J Alloys Compd* 253–254:1–9
- [4] Zakharkin LI, Gavrilenko VV (1962) The direct synthesis of sodium and potassium aluminum hydrides from the elements. *Dokl Akad Nauk SSSR* 145:793–796
- [5] Ashby EC, Kobetz P (1966) The direct synthesis of Na_3AlH_6 . *Inorg Chem* 5:1615–1617
- [6] Huot J, Boily S, Guther V, Schulz R (1999) Synthesis of Na_3AlH_6 and $\text{Na}_2\text{LiAlH}_6$ by mechanical alloying. *J Alloys Compd* 283:304–306
- [7] Wang P, Kang XD, Cheng HM (2005) Direct formation of Na_3AlH_6 by mechanical milling NaH/Al with TiF_3 . *Appl Phys Lett* 87:071911
- [8] Kircher O, Fichtner M (2005) Kinetic studies of the decomposition of NaAlH_4 doped with a Ti-based catalyst. *J Alloys Compd* 404–406:339–342
- [9] Zidan RA, Takara S, Hee AG, Jensen CM (1999) Hydrogen cycling behavior of zirconium and titanium–zirconium-

- doped sodium aluminum hydride. *J Alloys Compd* 285:119–122
- [10] Mao J, Guo Z, Liu H (2012) Enhanced hydrogen storage properties of NaAlH_4 co-catalysed with niobium fluoride and single-walled carbon nanotubes. *RSC Adv* 2:1569–1576
- [11] Adelhelm P, de Jongh PE (2011) The impact of carbon materials on the hydrogen storage properties of light metal hydrides. *J Mater Chem* 21:2417–2427
- [12] Léon A, Schild D, Fichtner M (2005) Chemical state of Ti in sodium alanate doped with TiCl_3 using X-ray photoelectron spectroscopy. *J Alloys Compd* 404–406:766–770
- [13] Bogdanović B, Eberle U, Felderhoff M, Schüth F (2007) Complex aluminium hydrides. *Scr Mater* 56:813–816
- [14] Singh S, Eijt SWH, Huot J, Kockelmann WA, Wagemaker M, Mulder FM (2007) The TiCl_3 catalyst in NaAlH_4 for hydrogen storage induces grain refinement and impacts on hydrogen vacancy formation. *Acta Mater* 55:5549–5557
- [15] Sandrock G, Gross K, Thomas G (2002) Effect of Ti-catalyst content on the reversible hydrogen storage properties of the sodium alanates. *J Alloys Compd* 339:299–308
- [16] Bastide J-P, Bonnetot B, Létoffé J-M, Claudy P (1981) Polymorphisme de l'hexahydroaluminate trisodique Na_3AlH_6 . *Mater Res Bull* 16:91–96
- [17] Bogdanović B, Brand RA, Marjanović A, Schwickardi M, Tölle J (2000) Metal-doped sodium aluminium hydrides as potential new hydrogen storage materials. *J Alloys Compd* 302:36–58
- [18] Weidenthaler C, Pommerin A, Felderhoff M, Schmidt W, Bogdanović B, Schüth F (2005) Evidence for the existence of $\beta\text{-Na}_3\text{AlH}_6$: monitoring the phase transformation from $\alpha\text{-Na}_3\text{AlH}_6$ by in situ methods. *J Alloys Compd* 398:228–234
- [19] Urbanczyk R, Peinecke K, Felderhoff M, Hauschild K, Kersten W, Peil S, Bathen D (2014) Aluminium alloy based hydrogen storage tank operated with sodium aluminium hexahydride Na_3AlH_6 . *Int J Hydrogen Energy* 39:17118–17128