



TEM characterization of pure and transition metal enhanced NaAlH₄

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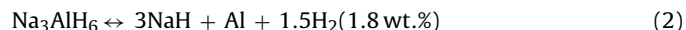
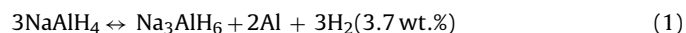
ABSTRACT

Possibilities and limitations in using transmission electron microscopy to characterize pure NaAlH₄ and transition metal enhanced NaAlH₄ have been investigated in detail. NaAlH₄ is extremely sensitive to O₂ and H₂O and must be handled under inert atmosphere at all times. Furthermore, it is highly unstable under the electron beam and only basic techniques such as diffraction contrast imaging and selected area diffraction that can be performed with a low flux electron beam can be used without the NaAlH₄ decomposing. By comparison, phases containing transition metal additive are very stable under the electron beam. The latter are investigated by a combination of high resolution imaging, electron diffraction and spectroscopy to determine distribution, composition, crystal structure and defect content in ball milled and hydrogen cycled, TiCl₃ and FeCl₃ enhanced NaAlH₄. It is demonstrated that a large amount of the added Ti or Fe is located at the surface of the NaAlH₄ grains as a combination of crystalline and amorphous Al_{1-x}TM_x (TM = Ti, Fe) nanoparticles.

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1. Introduction

A reliable method for reversible hydrogen storage is the key requirement for onboard use of hydrogen in transportation applications. Among the various approaches for hydrogen storage, complex hydrides are seen to be one of the most promising group of materials [1]. Pure complex hydrides are not considered as viable candidates for reversible hydrogen storage due to the high stability of the materials at operating conditions for fuel cells, and lack of H reversibility. However, in 1997 Bogdanovic and Schwickardi discovered that adding transition metals, such as Ti, to NaAlH₄ enabled reversible hydrogen absorption at moderate temperatures [2]. In addition, the kinetics of hydrogen reabsorption increased by several orders of magnitude. A theoretical storage capacity of about 5.5 wt.% H₂ can be reversibly released in a two step decomposition forming NaH and Al as the final products:



Since the discovery of adding Ti to NaAlH₄, numerous research groups have tried to optimize the parameters involved in reversible hydrogen storage with respect to kinetics and storage capacity.

However, further optimization depends on a thorough understanding of one fundamental question: what are the state, location and role of the added Ti during reversible hydrogen storage in NaAlH₄? The efforts made to solve this question span over a wide range of experimental techniques, including X-ray diffraction (XRD) [3–6], neutron diffraction [7], infrared (IR) and Raman spectroscopy [8], anelastic spectroscopy [9], differential scanning calorimetry (DSC) [10,11], electron paramagnetic resonance (EPR) [12], X-ray absorption spectroscopy (XAS) [13–15], X-ray photoelectron spectroscopy (XPS) [16–18], inelastic and quasielastic neutron scattering [19,20], nuclear magnetic resonance (NMR) [21,22], muon spin rotation (μSR) [23], scanning electron microscopy (SEM) [3,18,24], and transmission electron microscopy (TEM) [24–29]. In addition, numerous density functional theory (DFT) calculations have studied possible Ti substitution scenarios in the bulk and at the surface of NaAlH₄ [30–38].

While interest has expanded to further complex hydride systems, it is clear that the fundamental principles of the hydrogen storage behavior of these materials are still not fully understood, particularly the role of added transition metal. In this context, the NaAlH₄ system retains a fundamental interest as it is the most extensively studied, possessing only moderate stability.

Despite the massive amount of work put into the understanding of the catalytic effects of Ti, only a few conclusions have been drawn. It has been verified, both theoretically [30] and experimentally [5], that bulk substitution of Ti into NaAlH₄ is very unlikely. It is also clear, based on EPR [12], XPS [30] and XAS [15,26,39], that Ti is largely reduced to a metallic, zero-valent state during ball milling. However, any Ti containing phase is invisible to most experimen-

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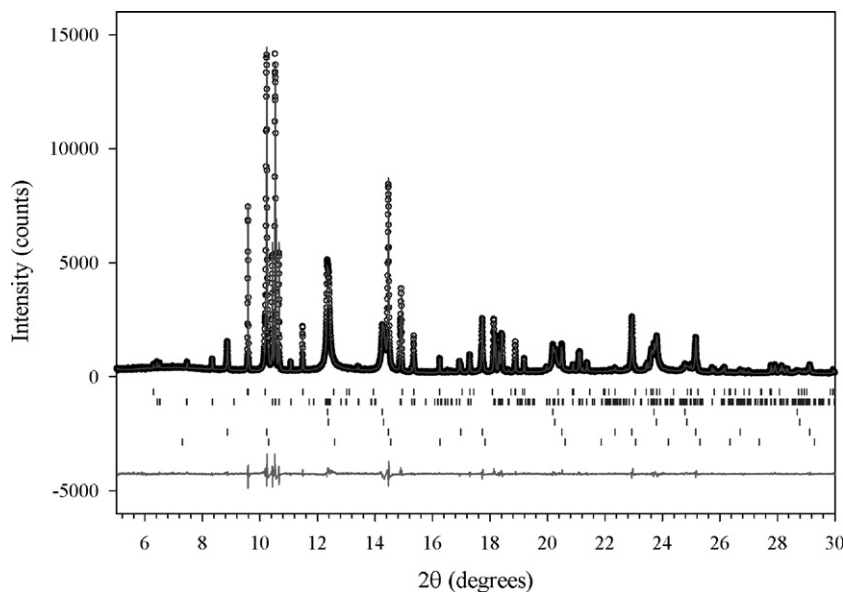


Fig. 1. High resolution X-ray synchrotron diffraction pattern of $\text{NaAlH}_4 + 0.1\text{TiCl}_3$ after two hydrogen cycles. Circles show the raw data, with the solid line showing the Rietveld model calculation. The difference profile below the pattern shows the fit quality. Reflection markers from top to bottom show NaAlH_4 , Na_3AlH_6 , Al, $\text{Al}_{85}\text{Ti}_{15}$, NaCl and Al_3Ti . Quantitative proportions of each phase are given in Section 2.

tal techniques. A few X-ray diffraction studies [5,6,40–42] show a shoulder on the high angle side of the Al reflections, which has been ascribed to the presence of crystalline Al_3Ti or $\text{Al}_{1-x}\text{Ti}_x$ phases, although these $\text{Al}_{1-x}\text{Ti}_x$ phases were not able to account for all of the added Ti. Besides metallic Ti and TiCl_3 additives, recent work has shown the direct addition of nanoparticles of TiO_2 (10 nm \times 40 nm) [43], TiN (6 nm) [44], TiB_2 (15–60 nm) [44], and microscopic TiC [45] to NaAlH_4 results in absorption/desorption kinetics at least as rapid as TiCl_3 additives. It is also observed by X-ray diffraction [43–45] that no interaction of these stable Ti containing phases occurs with NaAlH_4 , implying that the NaAlH_4/Ti containing phase interface is the local structure of most interest in understanding the role of Ti based additives in producing hydrogen reversible NaAlH_4 . The local morphology of how these additives are embedded in the surface of the NaAlH_4 grains is of fundamental interest, and the use of reliable and informative techniques to study these surface morphologies has been limited.

TEM is maybe the most versatile tool to characterize materials at the nanoscale. Phases and their crystal structures, interfaces and chemical compositions can potentially be analyzed down to the atomic scale. However, two problems have limited the use of TEM in the study of alanates, such as NaAlH_4 : (a) NaAlH_4 is highly unstable under the electron beam, and (b) it is a challenge to transport NaAlH_4 into the microscope without exposing the sample to O_2 or H_2O . In this work, the possibilities and limitations by using TEM to characterize NaAlH_4 and Ti and Fe enhanced NaAlH_4 are carefully described. Moreover, it is shown how composition, crystal structure and defects of the TM phases can be determined in detail by a combination of several TEM techniques. While contributing to the fundamental understanding of the NaAlH_4 –TM systems, the methodology described is expected to be relevant to studies of other hydrogen storage candidate materials and other air-sensitive systems. Understanding the role of the TM is a potential key to destabilizing higher wt.% and more stable hydrogen materials, such as for example LiBH_4 with a theoretical H storage capacity of 18.5 wt.%.

2. Experimental

NaAlH_4 was purchased from Albermarle Corporation (LOT NO. #:22470404-01, >93% purity), and TiCl_3 and FeCl_3 were purchased from Sigma–Aldrich Chemicals

(>99.99% purities). The powders were always handled under inert atmosphere in a dry Ar glove box. NaAlH_4 powders, pure or mixed with TiCl_3 or FeCl_3 , were prepared in 1 g quantities in a Fritsch P7 planetary mill, with ball to powder ratio of 20:1, and milled at 750 rpm for a period of 1 h. Hydrogen cycled powders (typically 140 °C/150 bar aliquot) were prepared in a Sieverts apparatus rated to 200 bar and 600 °C. Powders were removed after 2 or 5 H cycles for TiCl_3 and after 2 H cycles for FeCl_3 additives. All the studied materials were tetra hydrides, i.e. all materials loaded into the microscope were fully charged with hydrogen, being on the left side in Eq. (1). Powder X-ray diffraction data were recorded at the Swiss–Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Samples were contained in rotating 0.8 mm boron–silica glass capillaries. High resolution data ($\Delta d/d \sim 3 \times 10^{-4}$) were typically collected at 295 K between 5 and 35° 2θ , in steps of 0.003–0.030°, depending on the sample broadening. A wavelength of 0.4998 Å was obtained from a channel cut Si(1 1 1) monochromator. Typical X-ray synchrotron diffraction data of $\text{NaAlH}_4 + 0.1\text{TiCl}_3$ after two hydrogen cycles is shown in Fig. 1. Quantitative phase analysis yields phase mol fractions as $\text{NaAlH}_4:\text{Na}_3\text{AlH}_6:\text{Al}:\text{NaCl}:\text{Al}_{85}\text{Ti}_{15}:\text{Al}_3\text{Ti} = 8.5\%:16.8\%:7.5\%:25.0\%:40.1\%:2.1\%$. These phase mol fractions are consistent with those reported in [40] for $\text{NaAlH}_4 + 0.1\text{TiCl}_3$ after three hydrogen cycles. These phase proportions represent the exact state of the sample prior to TEM measurements.

Transmission electron microscopy was performed using a JEOL 2010F field emission microscope operating at 200 kV, or a Philips CM30 operating at 100–300 kV. All TEM samples were dispersed on thin, holey carbon film coated Cu grids inside the glove box and transferred into the column of the microscope by two different methods: (a) an oxygen tight transfer cover was used, with the cover being removed inside a glove bag attached to the holder entrance of the microscope. The glove bag was flushed with Ar (>99.999% purity) to prevent sample oxidation. (b) A Gatan environmental cell TEM holder was used. A vacuum gate valve on the environmental chamber allowed the sample to be withdrawn and isolated in the chamber during transfer, which prevented contamination or contact with air. The cell was evacuated by a turbomolecular-pump before being opened to the TEM vacuum. Electron diffraction patterns were integrated using the ProcessDiffraction V.4.2.4 B software package [46]. The inelastic background in the integrated diffraction patterns was subtracted by a combination of a four parameters exponential decay function and a third order polynomial.

3. Results and discussion

3.1. Decomposition and oxidation

NaAlH_4 is highly unstable under the electron beam, and this is clearly demonstrated by Fig. 2a–d. Fig. 2a shows an agglomerate of pure NaAlH_4 single crystals. These agglomerates decompose completely on a time scale of less than 5–30 s under a normal electron flux, 200 keV electron beam. The decomposition time depends on sample thickness, and on thicker sample areas it takes longer time

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