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Engineering improvement of $NaAlH_4$ system

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ABSTRACT

The significant engineering challenges associated with developing lower-pressure, materials-based, hydrogen storage systems for hydrogen fuel cell light-duty vehicles are being addressed by focusing on the role that powder consolidation can play. $NaAlH_4$ with 4 mol % $TiCl_3$ was selected as the model material. We focused on the changes in the physical (density and thermal conductivity) and mechanical properties (biaxial flexure strength) and on how these impacted the volumetric capacity of the hydrogen storage system. Both the thermal conductivity and the density of the ball milled material improved with applied pressure in a uniaxial press over the range of 14 MPa–281 MPa. The thermal conductivity reached a value of (1.64 ± 0.02) W/m/K, which was a factor seven higher than that of the unconsolidated powder. The volume of the material was reduced by 42% at the highest applied pressure. A method was developed for determining the strength of $NaAlH_4$ pellets before and after hydrogen absorption and desorption cycles. It is based on a biaxial flexure test that was originally designed for determining the strength of green ceramic materials. The tests showed that the pellets were strong with biaxial flexure strength of 1.4 kpsi which was unaltered over three studied hydrogen absorption/desorption cycles. The increased materials density did not affect the hydrogen absorption and desorption kinetics, which is important in order to benefit from the improved volumetric capacity. The new material properties of the compacted $NaAlH_4$ were used in finite element modeling of a hydrogen storage system that targeted a fast refueling time. The results clearly show an improvement of the volumetric capacity of the system by powder consolidation but the gravimetric capacity remains below target, as expected. A system level study of a light-duty vehicle with such a hydrogen storage system is required in order to determine whether the amount of hydrogen stored in the pore volume of the sodium alanate will still be enough to enable one cold start from room temperature to its operating temperature (120–140 °C) or that a buffer volume needs to be installed. While it is recognized that a sodium alanate based hydrogen storage system has its limitations, it has been demonstrated that powder consolidation can address some of those limitations by improving the thermal conductivity and volumetric capacity.

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Abbreviations: DSC, Differential Scanning Calorimeter; ENG, Expanded Natural Graphite; FWHM, Full Width at Half Maximum; GEM, General Effective Medium; HSECoE, Hydrogen Storage Engineering Center of Excellence; PCI, Pressure Composition Isotherm; SAH, Sodium Aluminum Hydride + 4 mol % TiCl3; TPS, Transient Plane Source.

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1. Introduction

On-board materials-based hydrogen storage systems for light-duty vehicles need to meet stringent targets in order to be able to compete with physical storage systems. A comprehensive set of such targets has been developed by the FreedomCAR and Fuel Partnership [1]. This set of targets serves as the technical targets of the Hydrogen Storage Engineering Center of Excellence (HSECoE). The HSECoE focuses on materials-based hydrogen storage systems that use on-board reversible metal hydrides, off-board regenerable chemical hydrides and cryo-adsorbents. All three DOE supported materials-based hydrogen storage centers of excellence have suggested promising materials to the HSECoE.

This paper focuses on the engineering of hydrogen storage systems with on-board reversible metal hydrides. Two targets that need improvement and are also amenable to improvements through engineering are the volumetric capacity of the system and the refueling time. The burden is now on the HSECoE to fill these gaps. Progress towards those targets will yield a hydrogen storage system with a new level of performance. It does require a priori that the material itself has a sufficient gravimetric capacity. Sodium alanate was suggested by the metal hydride COE as it is a well-defined material [2–9]. It was therefore selected for developing compaction techniques and modeling tools while monitoring progress in the development of better materials.

The results show that a hydrogen storage system based on sodium alanate cannot meet the gravimetric capacity target for light-duty vehicles, which is due to the limited gravimetric capacity of the sodium alanate material itself. It is anticipated that the progress that has been made in the engineering of this particular hydrogen storage system can be applied to other reversible metal hydride materials that have a higher gravimetric capacity, such as in the Li-Mg-N-H system [10].

2. Materials and methods

2.1. Experimental

The raw materials were commercial $NaAlH_4$ (Albemarle Corporation), $TiCl_3$ (Aldrich, Reagentplus™(>98.5%)), Aluminum (Alfa Aesar, 97.5%, spherical, APS 3.0–4.5 μm) and high purity Expanded Natural Graphite (SGL Carbon, $d_{50} = 6.9$ μm).

$NaAlH_4$ with 4 mol% $TiCl_3$ (hereafter abbreviated as SAH) was prepared in small batches by mixing 2 g of $NaAlH_4$ with 0.238 g of $TiCl_3$ in a Spex CertiPrep 8000-D Mixer Mill. The stainless steel vial had a 2.25" inside diameter and an internal height of 3". Two ½" and two ¼" stainless steel balls were used to agitate the mixture for a total of 3 h. The batches were combined into a larger container for further use.

Aluminum or Expanded Natural Graphite (hereafter abbreviated as ENG) was mixed with the catalyzed $NaAlH_4$ by rolling the mixtures in a 250 ml Nalgene bottle with fourteen 0.5" alumina balls for 1 h at about 50 rpm.

Samples were pressed uniaxially with either a cylindrical die (ID = 20 mm, Sperac) or a square die (20 x 20 mm, Across International) from the prepared powders with a manual hydraulic press (Sperac) with a range of 1–15 tons inside a glovebox filled with an inert and dry nitrogen atmosphere. The resulting density of the pressed pellets was determined from their weight and volume.

2.2. X-ray diffraction

X-ray powder diffraction was performed with a theta–theta Rigaku Ultima IV diffractometer equipped with a sealed Cu X-ray tube operated at 2.2 kW. X-ray diffraction was done in air through a DuraSeal™ film which sealed the sample in its glass holder with a 0.2 mm cavity. The Rigaku incident beam Cross Beam Optics was operated in the Bragg-Brentano Para-focusing mode. A D/teX-ULTRA High-Speed Position Sensitive Detector was positioned at a goniometer radius of 285 mm and operated at a count rate of about 10^6 cps/pixel. The pattern data were collected with a step size of 0.03° 2-theta per step at 2.0° 2-theta per minute in the continuous mode over the 2-theta range of 5–150°. The instrument was calibrated with NIST Si 640a to correct 2-theta deviations from the values found for FIZ #652255 (Si Standard Reference Material) and to correct for instrumental broadening effects on FWHM values as a function of the 2-theta angle. The K α-1/K α-2 ratio was determined by profile fitting & the number entered into the Jade + Preferences window. All data analyses were done with the Materials Data, Inc., Jade+, with the Search/Match and Whole Pattern Fitting (WPF) options, Version 9.1.1. Databases used were the FIZ/NIST Inorganic Crystal Structure Database (ICSD), Version 2010-1, and the International Centre for Diffraction Data (ICDD) PDF 2 Database, Version 2009. To apply the WPF/Rietveld analysis to a set of data, the 2-theta scale was corrected, all phases present were identified & associated with a pattern in the ICSD for which a Reference Intensity Ratio (RIR) was cited and all peaks from the DuraSeal™ film were removed. The non-linear least-squares optimization of the WPF routine then was used to fit the model to the observed data by varying the background, the FWHM of each phase from which average crystallite sizes were calculated, the lattice parameters of each phase & the weight per cent values.

2.3. Thermal conductivity

Thermal conductivity measurements were performed with a TPS500 Hot Disk Thermal Constants Analyzer, which is based on the Transient Plane Source (TPS) method [11]. The Kapton sensor and heating source had a diameter of 6 mm. The cylindrical samples had a diameter of 20 mm and a thickness > 10 mm. The bar shaped samples had a width and length of 20 mm and a height of 18 mm. The different samples were meeting the minimum sample size requirement for that sensor (diameter > 12 mm, thickness > 6 mm). The sensor was placed symmetrically between two identical sample pieces with the double spiral centred and totally covered. A sample holder was used to clamp the pieces firmly together. The sample holder was located inside an Argon filled MBraun LABmaster 130 glovebox in order to provide a dry and inert environment for testing the thermal conductivity of this pyrophoric SAH material at room temperature (21 °C). Measurement time and heating power were selected that

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