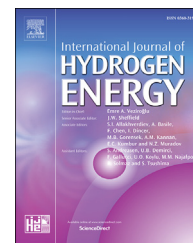


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Freeze-dried ammonia borane-polyethylene oxide composites: Phase behaviour and hydrogen release



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ABSTRACT

A solid-state hydrogen storage material comprising ammonia borane (AB) and polyethylene oxide (PEO) has been produced by freeze-drying from aqueous solutions from 0% to 100% AB by mass. The phase mixing behaviour of AB and PEO has been investigated using X-ray diffraction which shows that a new ‘intermediate’ crystalline phase exists, different from both AB and PEO, as observed in our previous work (Nathanson et al., 2015). It is suggested that hydrogen bonding interactions between the ethereal oxygen atom (–O–) in the PEO backbone and the protic hydrogen atoms attached to the nitrogen atom (N–H) of AB molecules promote the formation of a reaction intermediate, leading to lowered hydrogen release temperatures in the composites, compared to neat AB. PEO also acts to significantly reduce the foaming of AB during hydrogen release. A temperature-composition phase diagram has been produced for the AB-PEO system to show the relationship between phase mixing and hydrogen release.

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Introduction

Ammonia borane (AB, NH_3BH_3) is a highly promising candidate material to meet the US Department of Energy's targets for portable hydrogen storage systems owing to its excellent gravimetric hydrogen storage capacity of 19.6 wt% H_2 , low dehydrogenation temperatures (compared to other candidates), and encouraging progress in recycling the material [2].

Unfortunately, the commercialisation of AB has been hampered by its low melting point (114 °C [3]) which, when hydrogen is produced at proximate temperatures, results in a waxy foam that is difficult to contain in a practical device. Other solid-state hydrogen storage materials do not suffer

from such effects. Furthermore, an incubation period exists prior to hydrogen release, and volatile by-products ammonia, diborane and borazine are produced alongside hydrogen, which are known to poison the sensitive catalytic components of fuel cells.

To address these issues, researchers have sought to use nanostructuring and nanoconfinement techniques [4–10] and chemical additives such as metal-containing [11–17] and non-metal-containing [18–23] species to modify the hydrogen release properties of AB. Polymer composites stand out as a particularly attractive option, since polymers tend to be cheap, lightweight and easy to form. To date, poly(methyl acrylate) [24], poly(methyl methacrylate) [25], poly(vinyl pyrrolidone) [26] and polyacrylamide [27] have been employed

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successfully by combining confinement and chemical interactions between AB and oxygen-containing functional groups within the polymer, albeit with relatively low AB loadings (<50 wt%).

In recent work [1], it was demonstrated that co-electrospinning AB with high molecular weight polyethylene oxide (PEO), produced solid-state hydrogen storage composites with reduced hydrogen release temperatures, no incubation time and suppression of foaming, even in composites containing 75 wt% AB. Furthermore, a distinct crystal phase, different from both pure AB and PEO, was found to form when the two materials are intimately mixed in this way. This new phase was thought to contain significant hydrogen bonding between the protic hydrogen atoms on the nitrogen atom (N–H) in AB, and the ethereal oxygen atom (–O–) in the PEO backbone.

In this paper we present data collected for AB-PEO composites over the full range of compositions to demonstrate the relationship between the phase mixing behaviour of AB and PEO and the hydrogen release observed. We also demonstrate that a freeze-drying method from aqueous solutions can be used to attain the same intimate mixing of AB and PEO as achieved by co-electrospinning, with the added benefits of a robust manner of composite production and great potential for materials manufacture at industrial scales. It is shown that combining AB with PEO in this way eliminates foaming upon hydrogen release. These advances confirm that AB-PEO composites are extremely promising candidates for portable hydrogen storage applications.

Experimental

Materials

The materials used were PEO (molecular weight 2,000,000 Da) from Sigma Aldrich, containing 200–500 ppm butylated hydroxytoluene (BHT) inhibitor, ≤ 1 wt% alkalis and other metals, and 0.8–3.0 wt% SiO₂ impurities and AB from Minal Intermediates (quoted purity 99%). Both were used without further purification.

Composite preparation

AB-PEO composites were prepared with compositions ranging 0–100 wt% AB. Composites will be denoted AB_{*n*} hereafter, where *n* is the weight percentage of AB within the material. To illustrate, a sample denoted as AB₁₀ contains 10 wt% AB and 90 wt% PEO.

To synthesise the composites, PEO powder was mixed with deionised water for 3 days at room temperature using a magnetic stirrer. The solution was divided and the appropriate mass of AB powder added to produce different compositions by weight. These solutions were stirred at room temperature for 2 h, or until the AB was fully dissolved. The samples were then frozen in a laboratory freezer at –18 °C overnight and the water removed by freeze-drying with the condenser at –55 °C, until a chamber pressure below 50 mTorr was achieved. The samples were stored in sealed containers in air prior to use.

Analytical techniques

Thermal analysis was performed using a Mettler-Toledo combined thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) instrument, which was connected to an MKS Cirrus mass spectrometer (MS). Samples were ramp heated under argon between 35 and 200 °C at 1.2 °C/min, which is approximately equivalent to the heating regime used in the nuclear magnetic resonance experiments described below.

Room-temperature (RT) powder X-ray diffraction (PXRD) was done with a Stoe StadiP transmission diffractometer equipped with a Cu X-ray tube run at 40 kV, 30 mA and a Ge 111 monochromating crystal to give K α_1 radiation at $\lambda = 1.54056$ Å. Data were collected with a Dectris Mythen 1 K silicon strip detector scanned from 5° to 40° 2 θ stepped at 0.5° every 20 s. Data steps were 0.015° 2 θ . For indexing the intermediate phase, data were collected from 2° to 32° 2 θ at 20 s per step.

In-situ PXRD was performed using a Rigaku SmartLab X-ray flat-plate Bragg-Brentano diffractometer with a 9 kW rotating Cu anode at 45 kV and 200 mA, monochromated for K α_1 radiation with a double bounce 220 germanium crystal and data collected with a 1D silicon strip detector. Data were collected from 10 to 30° 2 θ with 0.01° steps every 2 °C intervals from 28 °C to 86 °C with a heating ramp between intervals of 2 °C/min. For both RT and *in-situ* PXRD, samples were rotated in the beam to improve powder averaging.

In-situ solid-state ¹¹B proton-decoupled magic angle spinning nuclear magnetic resonance (¹¹B{¹H} SS MAS-NMR) spectra were obtained at the EPSRC UK National Solid-state NMR Service at Durham. The spin rate used was 3 or 6 kHz, depending on the sample, with magnetic field 9.4 T (128.30 MHz). The measurements were two-pulse phase modulated (TPPM) proton decoupled at a field equivalent to approximately 60 kHz. Spectra were recorded at 10 °C intervals from 25 °C to 195 °C, and for the final products once the instrument had cooled to 25 °C at the end of the experiment. The heating rate was 2 °C/min between each measurement temperature step, and the spectra were recorded 8 min apart: 5 min for heating and 3 min for stabilisation.

Results and discussion

Freeze-drying aqueous AB-PEO solutions produces a white, porous, spongy material (Fig. 1). Materials with low AB content are more elastic and porous than those with higher amounts, due to the elasticity of the PEO component and the greater water content of the solution respectively. The plasticity of AB-PEO materials is useful since it permits the pressing, shaping, moulding and extrusion of the material into any form.

Phase mixing behaviour

Further to our previous work [1] the diffraction patterns of freeze-dried synthesised composites (Fig. 2) show three crystallographic phases present at room temperature: tetragonal AB [28], monoclinic PEO [29] and an unknown intermediate phase.

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