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Cyclic stability and structure of nanoconfined Ti-doped NaAlH₄

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ABSTRACT

NaAlH₄ was melt infiltrated within a CO₂ activated carbon aerogel, which had been pre-loaded with TiCl₃. Nanoconfinement was verified by Small Angle X-Ray Scattering (SAXS) and the nature of the Ti was investigated with Anomalous SAXS (ASAXS) and X-Ray Absorption Near Edge Structure (XANES) to determine its size and chemical state. The Ti is found to be in a similar state to that found in the bulk Ti-doped NaAlH₄ system where it exists as Al_{1-x}Ti_x nanoalloys. Crystalline phases exist within the carbon aerogel pores, which are analysed by *in-situ* Powder X-Ray Diffraction (PXRD) during hydrogen cycling. The *in-situ* data reveals that the hydrogen release from NaAlH₄ and its hydrogen uptake occurs through the Na₃AlH₆ intermediate when confined at this size scale. The hydrogen capacity from the nanoconfined NaAlH₄ is found to initially be much higher in this CO₂ activated aerogel compared with previous studies into unactivated aerogels.

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Introduction

Despite the extreme and exponentially increasing human energy consumption there is plenty of renewable energy available to us, but unfortunately these energy sources

strongly fluctuate over time and geography. The most difficult challenge appears to be the development of efficient and reliable long-term energy storage, over days, weeks and months [1]. Hydrogen is an excellent energy storage medium, with the highest gravimetric energy storage density. The low volumetric energy storage density of hydrogen gas can be

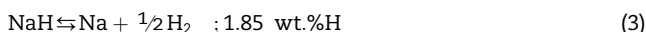
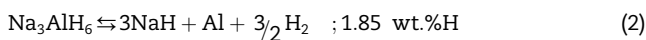
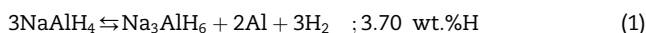
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greatly improved through its storage in a solid-state hydride. To date, NaAlH₄ is one of the most promising hydrogen storage compounds from a commercial stand point due to its low cost, moderate operating temperature and practical operating pressures. As such, ongoing research is focused on optimizing large scale NaAlH₄ tanks for energy storage applications [2,3]. It is well known that NaAlH₄ decomposes, releasing hydrogen in 3 steps:



The first two steps release 5.6 wt.% H at moderate temperatures, whilst the third step is not usually utilised due to its high temperature requirements (~400 °C). Fast and low temperature hydrogen release and absorption was first realised in 1997 [4] through the addition of a TiCl₃ additive. This seminal research initiated a plethora of experimental and theoretical studies into the catalytic mechanism of low temperature hydrogen release and uptake in NaAlH₄. The mechanism was only recently determined through a series of detailed and focussed experimental studies into doped NaAlH₄ [5–11]. The TiCl₃ is reduced by NaAlH₄, forming NaCl, Al, and a selection of Al_{1-x}Ti_x nanoalloys on the surface of the NaAlH₄ crystallites [5]. These Al–Ti nanoparticles provide dissociation sites for H₂ gas, increasing the kinetics of hydrogen absorption into decomposed NaAlH₄ [9]. The same Al–Ti nanoparticles can also influence the Al–H bonding to enable low temperature hydrogen release [9]. This bifunctional mechanism is the key to fast absorption and desorption kinetics in the NaAlH₄ system. The functionality of the Al–Ti nanoparticles is highly dependent on the morphology of the sample, where the Al–Ti must be in close contact with the NaAlH₄ whilst being accessible to H₂ gas [9]. This intimate contact may be manufactured and maintained through the process of nanoconfinement.

Nanoconfinement involves the incorporation of a compound within a porous framework. The framework controls the particle size of an incorporated compound by its pore size and also restricts long-range phase segregation during hydrogen release and uptake [12,13]. The importance of the CO₂ activation process in carbon aerogel synthesis was recently highlighted in regard to its advantages for nanoconfinement [14]. The CO₂ activation process reduced oxygen impurities from the scaffold whilst increasing the surface area. This means that the aerogel scaffold is less reactive towards oxygen-sensitive materials, allowing improved hydrogen capacity and better reversibility of nanoconfined hydrides. The reduction of functional groups from carbon aerogel during heat treatment and CO₂ activation is well known [15]. However, depending on synthesis conditions, some functional groups can still remain in the carbon aerogel after heat treatment to 1050 °C [16]. The cyclic stability of nanoconfined hydrides is not only related to the inertness of the scaffold. Significant levels of degradation in nanoconfined NaAlH₄ were recently observed [17] due to expulsion of reaction products from the scaffold under vacuum at high temperatures. However, this study relates to nanoconfinement

within an ordered mesoporous carbon, and the effect of pore ordering on confinement permanency is not yet known.

The investigation into nanoconfined TiCl₃ doped NaAlH₄ was recently conducted [18], demonstrating that it provided faster rates of hydrogen evolution than undoped nanoconfined NaAlH₄. However, in this study the carbon aerogel was not CO₂ activated during synthesis, leading to a low aerogel surface area (735 m²/g) and a high likelihood of reactive functional groups in the scaffold. In fact, there is a significant proportion of Al present after NaAlH₄ infiltration, indicating a reaction with the scaffold. This is further supported by the low hydrogen capacity achievable, only 2.9 wt.% H instead of the expected >5 wt.% H.

In the current study we aim to infiltrate TiCl₃ doped NaAlH₄ into a CO₂ activated carbon aerogel, limiting the degree of scaffold reactivity. We aim to investigate the cyclic stability of nanoconfined Ti-doped NaAlH₄ and also determine information about the state of the Ti-based additive in the nanoconfined system.

Material and methods

Aerogel synthesis

Carbon aerogel (CA) was synthesized according to a well-known method [19] from a resorcinol-formaldehyde pathway using a sodium carbonate catalyst. The reagents, resorcinol (41.791 g), formaldehyde (56.9 mL), and Na₂CO₃ (0.034 g) were stirred in water (56.6 mL) for 2 h. The mixture was then aged at room temperature for 24 h, 50 °C for 24 h, and then 90 °C for 72 h. The gels were then washed with acetone 3 times and dried in air overnight at room temperature. Next, the gels were pyrolysed under flowing nitrogen (50 mL/min) by heating from room temperature to 840 °C at 2.6 °C/min, holding for 6 h, and then cooling back to room temperature at 15 °C/min.

Activation of the aerogels was performed using CO₂ treatment to increase the total pore volume and surface area [15]. The aerogels were activated under flowing CO₂ (50 mL/min) during heating from room temperature to 920 or 940 °C, holding for 5.5 h, and then cooling back to room temperature at 15 °C/min.

Three different aerogels were synthesized as shown in Table 1.

After synthesis, all aerogels were degassed by heating to 400 °C under dynamic vacuum for several hours to remove traces of air and moisture from the porous framework. The degassed aerogels were then transferred into an argon

Table 1 – CO₂ activation parameters for as-synthesised samples.

Name	CO ₂ activated	Activation temperature (°C)	Material loss (%)
X	No	–	–
XA1	Yes	920	39.9
XA2	Yes	940	45.6

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