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# Experimental and theoretical study of compositional inhomogeneities in $\text{LaNi}_5\text{D}_x$ owing to temperature gradients and pressure hysteresis, investigated using spatially resolved in-situ neutron diffraction

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## ABSTRACT

An in-situ neutron investigation of the spatial variation in hydride composition of  $\text{LaNi}_5$  after a single absorption pressure step was performed. Compositional inhomogeneities are formed due to the strong temperature gradients created by the rapid absorption process coupled with the pressure and temperature hysteresis of the metal–hydrogen interaction. The hydride fraction of  $\text{LaNi}_5$  in a cylindrical cell was mapped using the ENGIN-X stress/strain instrument and quantitative phase analysis performed using the Rietveld technique. The material was observed to preferentially absorb hydrogen close to the edges of the cell where heat transfer out of the material was more efficient. This spatial variation was maintained even after thermal equilibration. The experimental results are compared to predictions of a 3D multiphysics model solved by the software package COMSOL. The good agreement achieved demonstrates the suitability of this model for optimisation of metal hydride tank systems.

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## Introduction

The increasing development of renewable energy supply systems, with an inherent sporadic output which is often dependent on weather conditions, such as photovoltaic and wind energy, requires the development of energy storage systems [1]. A hydrogen-based storage system has the potential to store excess energy as hydrogen during high output

periods and supply energy when the direct output drops below demand with the use of fuel cells [2–4]. To do this, the hydrogen must be stored until required.

Hydrogen storage research has been extensive, with a focus on vehicular applications [2,5,6]. For stationary applications however, such as smoothing the intermittent supply of renewable energy sources, requirements such as high gravimetric and volumetric capacities are less important [7]. Solid state hydrogen storage in hydrides and complex

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hydrides at moderate pressures is a safer and often cheaper and more convenient storage system than pressurised or liquefied gas, and a number of metal hydride (MH) tank systems have been built or proposed [4,8–10].

Hydrogen absorption by metal hydrides is an exothermic reaction, in some cases with quite large formation enthalpies [11]. As the temperature of the metal hydride bed rises, so does the equilibrium pressure of the material, necessitating higher pressures to maintain the absorption process, or removal of the heat to allow absorption at the initial applied pressure. The converse applies during desorption where the material cools and requires the addition of heat to maintain the release of hydrogen [12]. Thus for practical storage tanks, heat management is a significant issue and there have been many types of heat management systems designed for MH storage tanks [13–17].

The development and testing of new tank heating/cooling systems, particularly for medium to large scale tanks, is expensive and modelling offers a way to explore novel designs as well as to optimise parameters for a particular design. It is therefore important that such models accurately predict the pressure, temperature and reacted hydride fraction, both spatially and temporally. Testing the models under different operating conditions where the outcomes have been experimentally observed is a crucial part of the continuing improvement of MH tank models.

If sufficient hydrogen to hydride a significant fraction of the metal alloy in a MH tank is released into the tank over a short time interval, then during the hydrogen absorption the heat released in the exothermic reaction, coupled with the typically poor effective thermal conductivity of the metal hydride powder, leads to temperature gradients in the MH bed [18]. Although an active cooling system may be in effect, only those parts of the bed closest to the heat exchange system are effectively cooled. Any cooled, unreacted metal will absorb hydrogen faster than hotter regions due to the lower equilibrium pressure, leading to greater absorption where the material is actively cooled and corresponding less absorption where the material is at a higher temperature. Consequently, there will be a spatial variation of the reacted fraction ( $f$ , the proportion of the bed that is hydride) throughout the tank [18,19].

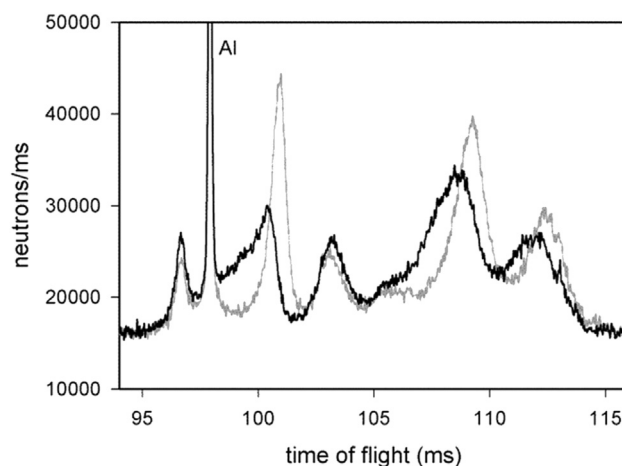
In the absence of hysteresis, and provided the isotherm exhibits a relatively flat plateau, as the material proceeds towards thermal equilibrium the low reacted fraction areas that are cooling will start to absorb more, lowering the pressure such that the high reacted fraction areas will release some hydrogen and ultimately the spatial inhomogeneity will disappear. Hysteresis occurs where the equilibrium pressure for a given composition or reacted fraction is different depending on the history of the reaction, typically observed as the plateau pressure of a pressure-composition-temperature (PCT) isotherm lying at a lower pressure for desorption than for absorption. This means that for a given temperature, a higher pressure is required for the system to absorb than is required for hydrogen release. Hysteresis is a well-known phenomenon in metal hydrides [7,12], although the exact origins are still uncertain.

In the case of a metal hydride that demonstrates hysteresis and is subjected to rapid hydrogenation, the spatial variation

of reacted fraction caused by temperature inhomogeneities does not disappear even after thermal equilibrium has been reached. This is because those areas which have a substantial reacted fraction do not release hydrogen because the pressure has not dropped below the equilibrium pressure for desorption. There is then insufficient pressure for further absorption for the unreacted areas even though they have cooled and, therefore, the spatial inhomogeneity is maintained [20].

A consequence of this is that measurements of the pressure-composition isotherm for a common intermetallic such as  $\text{LaNi}_5$  can yield very different results depending on the magnitude of the pressure step applied to the sample [21]. Compositional inhomogeneities due to temperature excursions was predicted and observed by Pons and Dantzer [18]. The effect was reviewed by Gray et al. [20] where it was found that the primary cause of this difference, termed the “large aliquot effect”, derives from the temperature gradients in the sample in conjunction with hysteresis. Kisi and Gray [19] observed a difference in the average reacted fraction for a small sample using neutron diffraction by masking out the centre of the neutron beam. This qualitatively indicates the spatial variation of reacted fraction in  $\text{LaNi}_5$ , but does not give quantitative information that would be suitable for modelling of large scale hydrogen storage tanks. Gray [22] obtained a neutron diffraction pattern for  $\text{LaNi}_5$  after a single absorption step which shows substantial peak broadening due to averaging over the mix of phases in the sample. This is reproduced in Fig. 1 and compared to a diffraction pattern for the same uptake, but approached in small steps approximately isobarically. Currently no spatially resolved experimental data on the compositional inhomogeneities in medium scale storage systems exists against which to test the capability of the different models.

The objective of this study was to experimentally map the spatial variation of hydrogen uptake due to the large aliquot effect described above, confirming previous studies and



**Fig. 1 – Neutron powder diffraction patterns for  $\text{LaNi}_5\text{D}_{0.36}$  (approximately the middle of the  $\alpha + \beta$  two-phase region) measured on HRPD at ISIS (UK). Grey line: pattern after pseudo-isobaric absorption steps. Black line: after a single isochoric step. A wide distribution of lattice parameters is apparent. Reproduced with permission from [22].**

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