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Optimization and comprehensive characterization of metal hydride based hydrogen storage systems using in-situ Neutron Radiography

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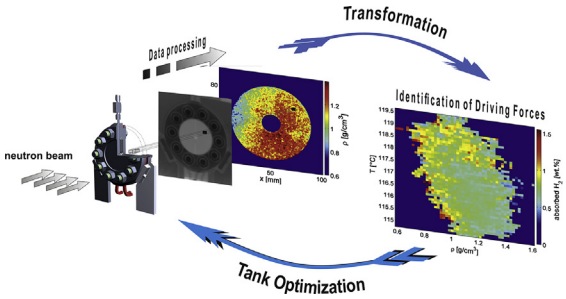
HIGHLIGHTS

- Hydrogenation of a sodium alanate compact studied by in situ Neutron Radiography.
- Quantification of spatial and time-resolved hydrogen distribution by a new method.
- Combination of macroscopic fields reveals the interdependency of driving forces.
- Unexpected and complex influence of material packing density on kinetics is derived.
- Correlation analysis allows for optimization of scaled-up metal hydride systems.

GRAPHICAL ABSTRACT



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ABSTRACT

For the storage of hydrogen, complex metal hydrides are considered as highly promising with respect to capacity, reversibility and safety. The optimization of corresponding storage tanks demands a precise and time-resolved investigation of the hydrogen distribution in scaled-up metal hydride beds. In this study it is shown that in situ fission Neutron Radiography provides unique insights into the spatial distribution of hydrogen even for scaled-up compacts and therewith enables a direct study of hydrogen storage tanks. A technique is introduced for the precise quantification of both time-resolved data and a priori material distribution, allowing inter alia for an optimization of compacts manufacturing process. For the first time, several macroscopic fields are combined which elucidates the great potential of Neutron Imaging for investigations of metal hydrides by going further than solely 'imaging' the system: A combination of in-situ Neutron Radiography, IR-Thermography and thermodynamic quantities can reveal the interdependency of different driving forces for a scaled-up sodium alanate pellet by means of a multi-correlation analysis. A decisive and time-resolved, complex influence of material packing density is derived. The results of this study enable a variety of new investigation possibilities that provide essential information on the optimization of future hydrogen storage tanks.

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1. Introduction

Hydrogen is considered as a very promising energy carrier for the future, both for mobile and stationary applications. Hence, within a recent study its high potential for grid storage has been shown by Pellow et al. [1]. In comparison to fossil fuels it combines the highest energy density per mass ($\approx$ 142 kJ kg^{-1}) with zero emissions except for water. Among other hydrogen storage possibilities, the usage of metal-hydrides has the advantage of highest volumetric densities [2]. Especially suitable for mobile applications are light metal hydrides because of their enhanced gravimetric capacity. The catalyzed complex metal hydride sodium alanate has been successfully reversed by Bogdanovic and Schwickardi and is one of the few examples of hydrides so far that combine moderate temperature of operation, good cycling stability and rather high capacity of 5.6 wt% [3]. For this reason, sodium alanate has been subject to several scale-up studies [4–6]. The use of metal hydrides for commercial hydrogen storage needs the transfer from lab-scale, basic scientific investigations to the study of scaled-up and application related systems. To tailor materials towards their theoretical capacity and towards application, there is a strong need for the possibility to investigate the hydrogenation process in operando. This enables the identification of the rate limiting steps and helps to overcome the slow kinetics that may be associated with them. Recently, in-situ Neutron Imaging has been identified as an extremely suitable and effective method for the characterization of hydrogen storage systems [7–10]. Due to the high neutron cross section of hydrogen in comparison to other elements, the in operando study of hydrogen distribution inside the metal hydride becomes possible. While first works have been based on the qualitative analysis only studying macroscopic structure deformations during application of pressure, there is a growing interest in a quantitative analysis [7–11]. Fundamental Beer's law and the ratio of images of one ab- or desorption sequence is used for the investigation of the hydrogen distribution. A major drawback concerning quantitative data evaluation is the uncertainty of the effective microscopic neutron cross section for hydrogen [8]. It depends on the sample detector distance in terms of the influence of scattering, the neutron beam spectrum and profile and for the use of thermal or cold neutron spectra also on potential Bragg scattering by structures of the metal hydride material and beam hardening effects [12,13]. So far, either literature values for the cross section of hydrogen or calibration measurements using water are used, both causing uncertainties in quantitative data [8,9]. In this paper we present a new method for a precise quantitative analysis by the combination of thermodynamic data and macroscopic attenuation as part of nuclear physics theory. Using a fission neutron spectrum, a compacted and scaled-up complex metal hydride, doped NaH–Al, was studied in operando in a storage tank made of steel. An investigation going further than solely imaging was our starting point to combine Neutron Imaging data for the hydrogen distribution with additional macroscopic fields. For hydrogen storage, the important fields are the temperature field as well as the material packing density distribution. We performed a unique and comprehensive correlation analysis between kinetics, temperature field and material packing density. This allows us to determine the relevant driving force in a complex, scaled-up system. For the sodium alanate system studied here, it reveals a dominant influence of the material packing density with less importance of variations within the external, steady-state temperature field. The dependency between kinetics and packing density is non-trivial and substantial for an optimal utilization of the material. The general approach in terms of a combination of Neutron Imaging data with additional macroscopic fields, which allows for spatial and time-resolved analysis of the inter-dependent driving forces in complex systems, is not limited for the study of scaled-up metal hydride systems, but applicable for Neutron Imaging of any scaled-up system in which hydrogen is the species of interest, e.g. in fuel cells.

2. Experimental

2.1. Sample preparation

Main raw materials were purchased from Sigma Aldrich (NaH) respectively Alfa Aesar (Al) with 99.95 % purity, additives ($3TiCl_3 + AlCl_3$)/3 were ordered from Acros Organics with 99.5 % purity respectively Graphite flakes were ordered from Alfa Aesar with 99.5 % purity and a median particle size of 7–10 μm. The mixture NaH + Al+0.05(($3TiCl_3 + AlCl_3$)/3) was ball-milled for in total 10 h using a common industrial tube vibration mill as described by Eigen et al. [14]. After 7 h of milling 0.05 wt% Graphite flakes were added for increase of thermal conductivity and milling was continued for 3 h. For compaction of material (formation of pellets), a 185 ton manual hydraulic press was used. The pellet (50 g) dimensions are ⌀ 77 mm (outer diameter) and ⌀ 12 mm (inner diameter) with a thickness of 10.5 mm. Additionally to the pellet, a sample of loose powder (30 g) was prepared from the same batch. All sample preparations were carried out inside a glove box under controlled argon atmosphere (H_2O and O_2 < 10 ppm). A stainless steel tank was designed and built particularly for in-situ Neutron Imaging investigations for temperatures of maximal 450 °C at pressures of maximal 150 bar. The sealing against ambient atmosphere was ensured by use of a FFKM o-ring. The pellet was placed upright in the tank. The wall thickness in this area is 24 mm in total. The inlet for hydrogen gas is in the center of the tank. For reasons of temperature gradient reduction for external temperature field, a thermal insulation is applied except for the region of interest where the neutron beam is penetrating the region of the tank volume storing the metal hydride.

2.2. IR-Thermography of storage tank

IR-measurements of the steel tank using a FLIR-i40 thermal imaging infrared camera were performed for characterization of the external temperature field. In the region of interest the tank hull was covered with a thermal conduction foil, a continuous temperature field was measured during the hydrogen absorption under the same conditions as described in the following section. IR-data was matched with data obtained by two temperature sensors in the inner body of the steel tank.

An IR-image of the whole steel tank covered by insulation during temperature increase is shown in the left part of Fig. 1. The steel tank surface in the center, which is the region of interest containing the pellet, is not covered by insulation to ensure a maximal neutron beam transmission. Its surface temperatures are much higher than the upper contrast boundary of 60 °C and cannot be resolved in the contrast range of the left part of Fig. 1. To enhance the low IR-emissivity of the tank surface area in the region of interest, the surface is covered by thermal conduction foil. The derived temperature field by IR-Thermography is shown for thermal equilibrium in the right part of Fig. 1. In first approximation this temperature field represents the temperature field inside the metal hydride pellet. Field characteristics and the use for correlation studies are further discussed in the results section.

2.3. In situ Neutron Imaging measurements

First time in-situ Neutron Imaging measurements of the hydrogen absorption of complex hydride pellets and powders were