Experimental report

24/05/2022

Proposal: **5-24-689**

Council: 4/2021

Title: In situ neutron powder diffractioninvestigation of structural changes in confined NaAlD4/carbon composites during cycling

Research area: Materials

This proposal is a resubmission of 5-24-662

Main proposer: **Rasmus PALM**

Experimental team: Sebastian JOHNSEN
Rasmus PALM

Local contacts: Thomas HANSEN

Samples: NaAlD4
NaAlD4/microporous carbon
NaAlD4/mesoporous carbon

Instrument	Requested days	Allocated days	From	To
D20	5	3	28/05/2021	31/05/2021

Abstract:

Nanoconfinement of hydrides inside a porous scaffold material is a perspective method to lower the release temperature, improve the release and absorption kinetics of H2 and prevent the segregation of decomposition products during H2 release. In this proposal in situ neutron powder diffraction of NaAlD4 confined in/on carbon scaffold materials is proposed. Two different scaffolding materials and bulk NaAlD4 will be used and the structural changes during desorption/absorption of D2 will be determined. The two scaffold carbon materials are chosen to be microporous and mesoporous to determine the influence of the carbon materials porosity on the confinement of NaAlH4. From these data the segregation of decomposition products and and the formation of amorphous and/or smaller crystallites during cycling will be determined. The results will be used to better design and optimize further complex metal hydride/carbon composites.

In situ neutron powder diffraction investigation of structural changes in confined $NaAlD_4$/carbon composites during cycling

Scientific background and aim of this experiment

Nanoconfinement of hydrides inside a porous scaffold material is a perspective method to lower the release temperature, improve the release and absorption kinetics of H_2 and prevent the segregation of decomposition products during H_2 release.[1-3] The vast lowering of the temperature of hydrogen release from $NaAlH_4$ nanoconfined in near nanometre pores has been shown by Balde et. al.[4] Also, the formation of amorphous and/or very small crystallites during dehydrogenation/hydrogenation cycles of confined $NaAlH_4$ has been shown.[5] As the particulate/crystallite size influences the T and p conditions of H_2 release and uptake to a high degree, the influence of confinement in/on different scaffold materials during multiple application cycles is of high interest.

The main aim of this experiment was to determine the segregation of decomposition products (primarily Al) and reformation of confined $NaAlD_4$ and the influence of the confinement on the processes. Thus, *in situ* neutron powder diffraction (NPD) measurements of bulk $NaAlD_4$ and $NaAlD_4$ confined on/at two carbon materials with different porosities and morphologies were planned and applied for. Unfortunately, the days of applied for beam-time was not acquired (3 days instead of the asked 5 days) because of high competition for the beam-line. In addition, the experiment was performed over the weekend, where the technician was not available for a sample change. Thus, only one composite, a $NaAlD_4$ confined on/at mesoporous nanoparticulate carbon material, was investigated during the measurement, but with a more stringent experimental routine. The aim of the *in situ* NPD measurements was to yield direct information about the scaffold materials' capability to confine the decomposition products, and thus, hinder the segregation of decomposition products into separate phases. In addition, with the use of *in situ* NPD it was possible to determine at what p and T conditions the deuteration of the material starts and how much does the confinement inhibit the formation of larger crystallites.

The measured $NaAlD_4$/carbon composite uses a nanoparticulate (~100 nm) carbon scaffolding material with a substantial amount of mesopores (most pores > 2 nm). Considerable H_2 released at $T \leq 150$ °C was determined in case of the used composite, even with a high loading of $NaAlH_4$, 60wt%, (Figure 2). Powder X-ray diffraction, gas adsorption, H_2 release measurements and deuteration were performed beforehand. Deuteration of the sample, increasing the real loading from 60 wt% in case of $NaAlH_4$ to 62 wt% in case of $NaAlD_4$, was used to increase the coherent scattering, and thus, make NPD measurements of the composites viable.

Experimental routine:

Measurements were performed on D20 with incident neutron wavelength of 1.54 Å through the use of Ge moderators (115) reflection at 90°. Empty sample holder under vacuum was measured in the T range from 300 K to 450 for background subtraction and assignment of Bragg peaks caused by the sample holder. The $NaAlD_4$/C sample was prepared in an inert gas filled glovebox. The sample was hermetically sealed in Ar atmosphere for transportation and connection to the sample stick. Four heating, D_2 dosing, and cooling cycles were performed (Table 1). Data reduction and initial analysis was done with OriginPro 2021b software package and batch Rietveld refinement with Topas software packages.

Table 1. Experimental routine

First cycle	Second cycle	Third cycle	Fourth cycle
Heat from 300 K to 450 K in steps of 30 K, stay at each step for 30 min	Heat from 300 K to 420 K in steps of 30 K, stay at each step for 30 min	Heat from 300 K to 450 K in steps of 30 K, stay at each step for 30 min	Heat from 300 K to 450 K in steps of 30 K, stay at each step for 30 min
Cool down to 430 K and dose 20 bar D_2	Dose 70 bar D_2 at 420 K	Cool down to 430 K and dose 75 bar D_2	Hold at 450 K for 3 h to achieve complete decomposition
Cooling to 300 K in steps of 30 K under D_2 loading	Cooling to 300 K in steps of 30 K under D_2 loading	Cooling to 300 K in steps of 30 K under D_2 loading	Cooling to 300 K in steps of 30 K
Vacuum sample holder	Vacuum sample holder	Vacuum sample holder	

Experimental results:

Successful deuteration (over 90%) of crystalline $NaAlH_4$ into $NaAlD_4$ was verified by Rietveld refinement and the composition of bulk crystalline material was determined at all experimental conditions. The presence and content of $NaAlD_4$, Na_3AlD_6, NaD, and Al was determined at all experimental T and p_{D2} conditions (Figure 1). Based on this the influence of the mesoporous carbon black on the decomposition and deuteration conditions was determined and analysed. The D_2 release at lower T-s and the absorption processes supporting reversible de(deuteration) from the composite have been analysed and a manuscript based on the experimental results has been submitted to the International Journal of Hydrogen Energy and is at the moment of uploading the final report under review.

Further plans:

As only one composite was measured because of the limited beam-time allocated for the proposal, additional measurements with composites using the proposed microporoous carbon scaffold material are planned. Hopefully to be performed at ILL, when the reactor is operational again.

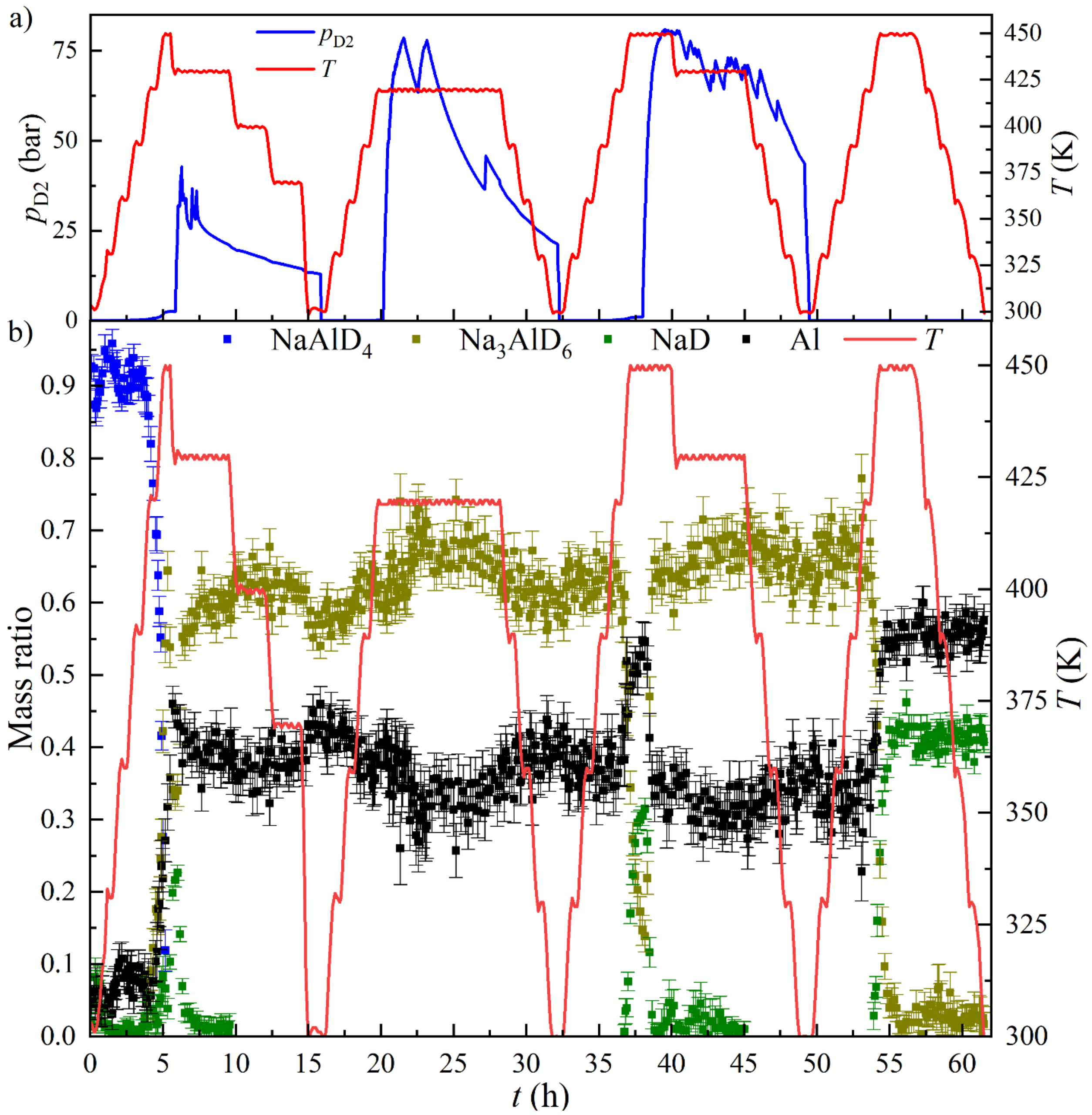

Figure 1. a) D_2 pressure, p_{D2}, and temperature, T, applied over the whole experimental routine and b) the crystalline phase composition of the sample acquired from Rietveld refinement and from which the diffraction caused by the scaffold carbon black has been subtracted,

References:

[1] C.P. Baldé, B.P.C. Hereijgers, J.H. Bitter, K.P. de Jong, Angew. Chem. 118 (2006) 3581–3583.
[2] S. Zheng, F. Fang, G. Zhou, G. Chen, L. Ouyang, M. Zhu, D. Sun, Chem. Mater. 20 (2008) 3954–3958.
[3] J. Gao, P. Adelhelm, M.H.W. Verkuijlen, C. Rongeat, M. Herrich, P.J.M. van Bentum, O. Gutfleisch, A.P.M. Kentgens, K.P. de Jong, P.E. de Jongh, J. Phys. Chem. C 114 (2010) 4675–4682.
[4] C.P. Balde, B.P.C. Herejigers, J.H. Bitter, K.P. de Jong, J. Am. Chem. Soc. 130 (2008) 6761-6765.
[5] R. Palm, H. Kurig, J. Aruväli, E. Lust, Microporous Mesoporous Mater. 264 (2018) 8-12.