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Final report on full characterization of D1.9-1.10 materials

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Deliverable D 1.11 (M 36) Report on full characterization of D 1.9 - 1.10 materials

A. Report on full characterization of D 1.9 materials: optimised porous carbon samples

Summary

Various porous carbon scaffolds have been examined as a support of the complex hydride material for the laboratory test tank for NANOHy project in the period between M24-M36. One of the important parameters of an ideal carbon scaffold is the large micropore volume, which decides the final hydrogen storage capacity of the nanocomposite material. The commercial material ACF25 has been proven very promising material after modification in our laboratories as described in the report M24 D1.8. In order to optimise micropore volume of ACF25, the procedures to widen the pore size using Boudouard reaction have been attempted by the Future Carbon GmbH. Additionally, another activated carbon IRH33 has been kindly provided by the *Institut de recherche sur l'hydrogène, Canada,* which has a larger micropore volume (~ 1.2 cm³/g) than other carbon scaffolds used in the project.

Experimental details

Further activation of ACF25

Boudouard reaction is a general method to activate the carbon material, e.g. widen the pore size and increase the pore volume.

$$CO_2 + C \leftrightarrow 2CO$$
, $\Delta H = +172.45$ kJ/mol

Several ACF25 samples have been treated at the temperature from 630° C to 660° C for 0.5 to 1.5 hours in an atmosphere of flowing CO₂ gas. Weight losses between ~ 3% and ~ 31% depending on material and conditions have been achieved. However, the surface and porosity analysis (BET) show no significant change of the pore volume after the treatment by CO₂ on ACF25 as shown in the Figure A.1. This might be due to the graphitic character and the uniform porosity of ACF25, which lead just to loss of material instead of widening of the pores by the treatment of CO₂.



Figure. A.1. Pore size distribution and total pore volume of ACF25 treated with CO₂

Activated carbon IRH33

IRH33 is produced by CO_2 activation of a carbonaceous material, which is provided by the Institut de recherche sur l'hydrogène (IRH) at the université du Québec à Trois-Rivières, Canada. IRH33 was ground with the mortar and pestle to get the fine powder material. The physisorption measurement of IRH33 revealed a BET surface area of 2587 m²/g and a micropore volume about 1.2 cm³/g.



Figure. A.2. N₂ Physisorption Isotherms (77K) of IRH33



Figure. A.3. Pore size distribution and total pore volume of IRH33.

B. Report on full characterization of D 1.10 materials: optimised complex hydride samples

Summary

Several complex hydrides have been synthesized and investigated for the NANOHy project in the past years. One of the targets of the project is to make a technical progress in developing bulk amounts of nanocomposite material with improved properties. Based on the properties of the complex hydride materials, wet incipient impregnation and melting infiltration techniques for preparing the nanocomposites have been developed as described in the report M24 (D 3.3). In the period between M24 and M36, the decision for an optimised complex hydride for a laboratory test tank was made. NaAlH₄ is one of the very few reversible hydrogen storage systems and can readily be infiltrated in carbon scaffolds by heating under H₂ pressure by the melting procedures. The nanoconfined NaAlH₄ shows significantly changed thermodynamic and improved kinetic properties as reported in D 4.1 and D 4.2. Hence, NaAlH₄ has been chosen as the complex hydride for the laboratory test tank for NANOHy project.

Additionally, the development of new complex hydride has been continued in the period between M24 and M36. The mixed boron hydride $LiBH_4/Mg(BH_4)_2$ with a eutectic melting point and the corresponding isotopic compounds $Li^{11}BD_4/Mg(^{11}BD_4)_2$ and $^7Li^{11}BH_4/Mg(^{11}BH_4)_2$ have been synthesised and characterised.

Experimental details

NaAlH₄

NaAlH₄ was used as purchased. NaAlD₄ was synthesized and characterized for the neutron diffraction studies like Small-Angle Neutron Scattering (SANS). The deuterides NaAlD₄ was prepared by cycling NaAlH₄ thrice under deuterium atmosphere. NaAlH₄ (with 2 mol% Ce catalyst) was cycled at 150 °C, 0.2 bar (desorption) and 125 °C, 100 bar of D₂ (absorption) in order to exchange the protium by deuterium. The purity of the products was examined by powder XRD and the sufficient degree of deuteration confirmed by IR spectroscopy. The structure of NaAlD₄ is identical to the one of NaAlH₄, see Figure B.1. Figure B.2 shows that more than 90% of the H was successfully exchanged by D in the material.



Figure B.1 XRD spectrum of pure $NaAIH_4$ and $NaAID_4$ obtained by cycling $NaAIH_4$ under Deuterium atmosphere.



Figure B.2 IR spectrum of NaAlD₄ obtained by cycling NaAlH₄ under deuterium atmosphere.

Mixed LiBH₄/Mg(BH₄)₂

The mixed LiBH₄/Mg(BH₄)₂ system with different compositions has been synthesised by ball milling. The mixture of LiBH₄ and Mg(BH₄)₂ with a molar ratio 1:1 has been found to be the eutectic composition exhibiting a eutectic melting at 180 °C as shown in Figure B.3.



Figure B.3 DSC profile of the mixed LiBH₄/Mg(BH₄)₂

The physical mixture has been investigated by using X- ray powder diffraction, solid sate NMR and thermal analysis. Figure B.4 shows the XRD patterns of the mixed $LiBH_4/Mg(BH_4)_2$ with molar ratio of 1:1 obtained after ball milling the starting materials. Some reflections can be assigned to the constituent phases but the broaden signals indicate the low crystallinity of the sample.



Figure B.4 The XRD patterns of the mixed LiBH₄/Mg(BH₄)₂ and the single phases

Furthermore, we have performed solid state Magic Angel Spinning (MAS) Nuclear Magnetic Resonance (NMR) measurements for the ¹¹B in this LiBH₄/Mg(BH₄)₂ system. As shown in Figure B.5, the mixed LiBH₄/Mg(BH₄)₂ interestingly shows only one single chemical shift at δ = – 36 ppm, which is different from any the reference spectra of pure LiBH₄ and Mg(BH₄)₂. This would suggest that the LiBH₄/Mg(BH₄)₂ after ball milling might be a solid solution. Further efforts will be taken to proof this characterisation.



Figure B.5 The solid state ¹¹B MAS-NMR spectra of LiBH₄/Mg(BH₄)₂