

Reversibility of the hydrogen desorption from LiBH₄: a synergetic effect of nanoconfinement and Ni addition

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Supporting information

Experimental Details

Carbon-supported Ni nanoparticles were prepared by incipient wetness impregnation following a literature procedure¹. Briefly, nickel nitrate (99%, Acros) and citric acid (99.5%, Acros) were mixed in a 3:2 molar ratio in demineralized water resulting in a bright green nickel citrate solution. Typically, 0.7 ml of the solution was added to 1g high surface area graphite (HSAG 500) under static vacuum. HSAG 500 is high purity (99.9%) graphitic carbon from Timcal Switzerland. It contains mesopores (mostly 2-3 nm) up to 20 nm in diameter, 500 m² g⁻¹ BET surface area and a total pore volume of 0.66 cm³ g⁻¹. The impregnated sample was dried in air overnight at 120 °C, calcined by heating to 450 °C under N₂ flow and reduced in a flow of a gas mixture of 5% H₂ in N₂ with 1 h dwell at 400 °C.

LiBH₄ (Acros-organics 95% pure) was incorporated into the Ni-impregnated carbon by melt infiltration method. The required amounts of Ni/C naocomposites and LiBH₄ were mixed in a graphite sample holder and placed into a stainless steel autoclave. An initial pressure of 75 bar H₂ was applied and the sample was heated at 3 °C min⁻¹ to 295 °C and allowed to stay for 30 min at 295 °C at a final pressure of ≈ 150 bar H₂. The sample was then allowed to cool down to room temperature, the hydrogen gas was released and the samples stored in the glove box. Apart from Ni impregnation, all other sample handling and storage was conducted under Ar atmosphere in a glove-box (contamination typically less than 1 ppm of O₂ and H₂O). Sample characterization was performed using X-ray diffraction (XRD), N₂- physisorption, and transmission electron microscopy (TEM) measurements. All measurements (except TEM) were done in air tight sample holders. XRD patterns were obtained at room temperature from 18 to 75° 2θ with a Bruker-AXS D-8 Advance X-ray diffractometer setup using CoKα_{1,2} radiation with λ= 1.79026 Å. The Ni crystallite size was determined by analyzing the 52.2° 2θ diffraction peak using the Debye–Scherrer method and assuming a Scherrer constant of 0.94. N₂-physisorption measurements were performed at -196 °C, using a Micromeritics Tristar 3000 apparatus. The pore size distributions of the samples were calculated from the desorption branch using

BJH theory with the Harkins and Jura thickness equation. TEM measurements were obtained using a Tecnai 20 microscope operating at 200 kV. Crystallite size histograms were determined by analyzing dark-field images and the average size determined from measuring 100-200 crystallites.

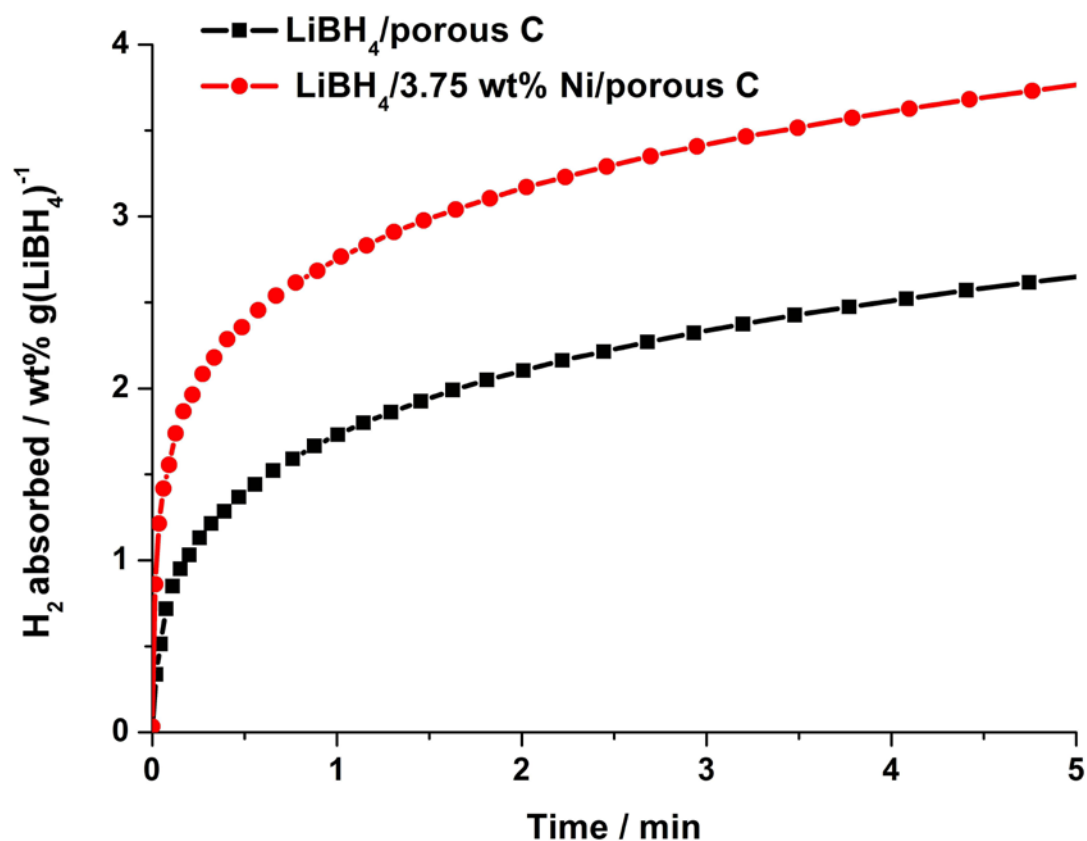
Hydrogen release properties of the nanocomposites was measured by temperature programmed desorption (TPD) using a Micromeritics AutoChem II 2920 apparatus. 100 to 150 mg of sample was heated at 5 °C/min from room temperature to 400 or 450 °C in 25 ml min⁻¹ Ar flow with a dwell time of 25 min at the maximum temperature. The composition of the desorbed gas was analyzed using quadrupole mass spectrometer (MS) with purified Ar as carrier gas. Rehydrogenation of the desorbed samples was performed in an autoclave by heating at 2 °C min⁻¹ with initial pressure of 20 bar H₂ to 320 °C and dwelling at 320 °C for 120 min at a final pressure of 40 bar. The amount of H₂ absorbed by the sample was determined by doing a second TPD experiment. Hydrogen release and uptake measurement was also performed in a magnetic suspension balance from Rubotherm. About 100 mg of the sample was loaded in a graphite sample holder and inserted into the Rubotherm sample holder. The sample was heated at 5 °C min⁻¹ to 400 °C under 1 bar Ar pressure (99.99 % purity). Rehydrogenation of desorbed sample was performed at 320 °C by increasing H₂ pressure from 1 bar to 40 bar in 40 min and remaining at 320 °C for 120 min. Hydrogen uptake and release were determined from the weight changes while correcting for buoyancy. Kinetic adsorption measurements were done using a fully automated manometric Sievert type apparatus (PCTPro-2000, Hy-Energy & Setaram, pressure measurement accuracy: 1% of reading). The measurements were performed on approximately 100 mg of the sample at 330 °C and initial reservoir pressure of 28 bar.

1. R. Bogerd, P. Adelhelm, J. H. Meeldijk, K. P. de Jong and P. E. de Jongh, *Nanotechnology*, 2009, **20**, 204019.

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Manometric (Sievert) hydrogen uptake measurement

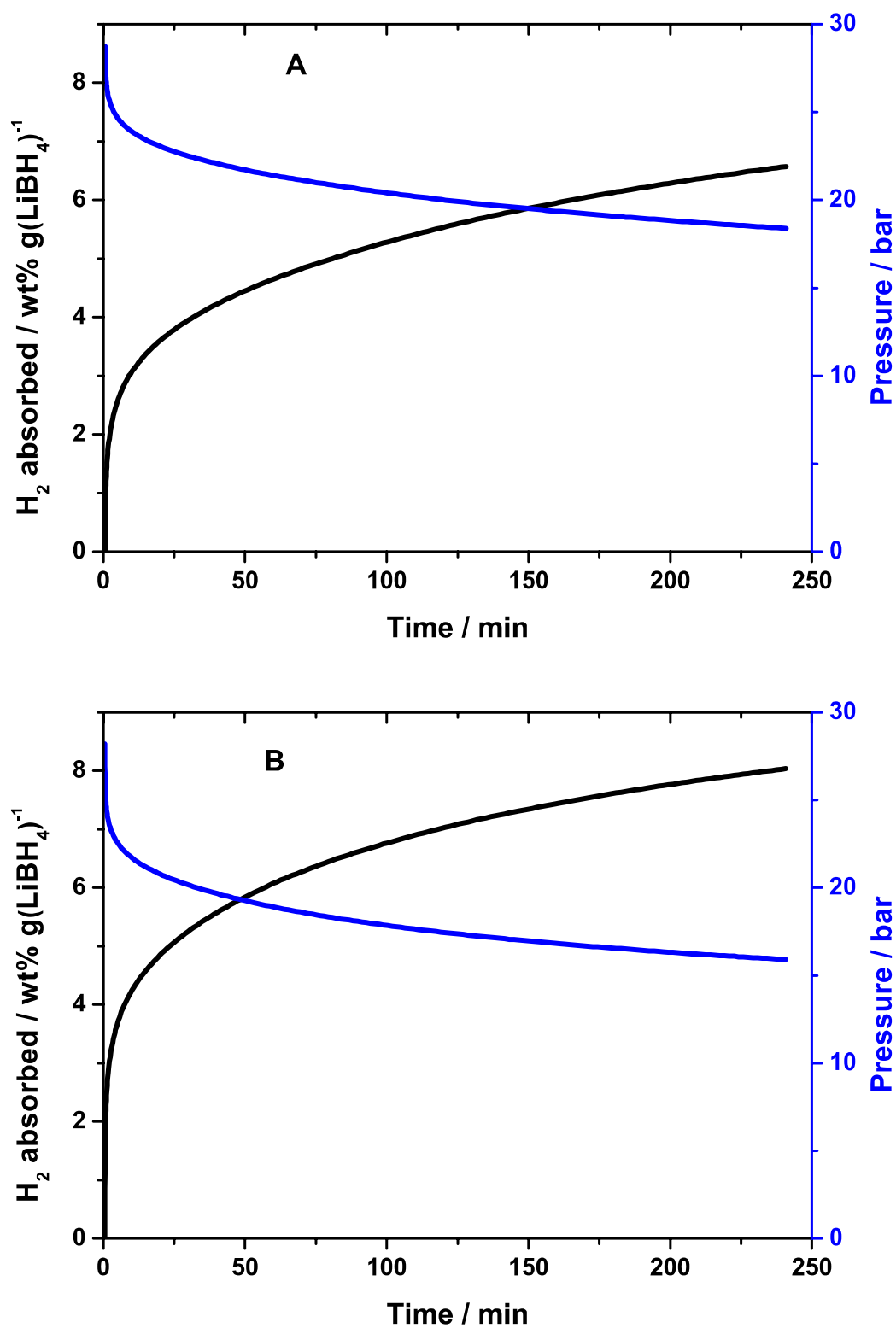


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Fig. S1: Manometric hydrogen uptake curves for 25 wt% LiBH₄/C nanocomposites with and without Ni. The measurement was done at 330 °C and an initial pressure of 28 bar H₂. The figure shows a very fast initial uptake (with 2.5 wt% H₂ absorbed within the first 5 min in the absence of Ni, and 3.7 wt% absorbed within 5 min in the presence of Ni).

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5 Fig. S2: Hydrogen absorption versus time, also indicating the resulting reservoir hydrogen pressure for (A) 25 wt% $LiBH_4$ /porous carbon (B) 25 wt% $LiBH_4$ /Ni/porous carbon nanocomposites.