**Experimental**

All sample preparations were done in an argon-filled glove box equipped with a recirculation system to keep the water and oxygen concentrations below 1 ppm. Chemical operations were performed on the bench under Ar (purity 99.9999 %) using Schlenk techniques.

**Preparation of the MgH\(_2\)/ACF nano composite**

Bu\(_2\)Mg solution was added drop wise to pre-treated ACF in a Schlenk flask and kept at room temperature for 0.5 hour, then cooled down to – 78°C with liquid nitrogen to shrink any gas volume in the sample and to draw the the Mg precursor into the pores of the carbon. After keeping this temperature for 1 hour the solvent was removed under a fine vacuum at gradually increased temperature for 5 hours. The procedures of impregnation/drying were successively performed with 1.5 ml of solution for each step to prevent excess Bu\(_2\)Mg from sticking on the surface of the carbon material. After total 12 ml of Bu\(_2\)Mg solution was added to 1.2 g of ACF and dried, the composite was hydrogenated by heating up to 180 °C under 60 bar of H\(_2\) in a autoclave type of reactor. Finally the prepared composite containing 22 mass% of MgH\(_2\) was ground in a mortar for further investigations. After total 12 ml of Bu\(_2\)Mg solution was added to 1.2 g of ACF and dried, the composite was hydrogenated by heating up to 180 °C under 60 bar of H\(_2\) in a autoclave type of reactor, according to the following equation.

\[
\text{Bu}_2\text{Mg}/\text{ACF} \xrightarrow{\text{60 bar } \text{H}_2, \text{230 } ^\circ\text{C}} \text{MgH}_2/\text{ACF} + \text{butane}
\]

The occurrence of exothermal hydrogenation of Bu\(_2\)Mg at 172 °C was monitored in DSC experiments by heating up the Bu\(_2\)Mg/ACF composite (Fig. S1) under hydrogen pressure. In order to prevent any evaporation of Bu\(_2\)Mg out of the cages of the carbon scaffold, 60 bar of H\(_2\) was applied during the synthesis step in the autoclave and the temperatures between 230-260°C for 10 hours were found to be the best conditions to get small sized MgH\(_2\) particles. In order to enable Bu\(_2\)Mg to be completely transformed to MgH\(_2\), the hydrogenation process was repeated for 3 times by removing the mixture gas of H\(_2\) and released butane from the reaction, subsequently adding fresh hydrogen again.
Preparation of ball-milled MgH$_2$/carbon samples

0.3 g of commercial MgH$_2$ and 2 g of graphite or activated carbon fiber (ACF) were ball milled for 6 hours under an argon atmosphere in a planetary ball mill (Retsch PM400) with hard stainless steel vial and stainless balls (ball-to-powder ratio of 30:1) with a speed of 300 rpm.

Sample characterization

Porosity characterisation of carbon material and prepared composites

The porosity of the carbon scaffolds and the prepared MgH$_2$/carbon composites was determined by nitrogen adsorption method and analysed by using BET (Brunner-Emmett-Teller) method. Physorption isotherms were collected on a micrometrics ASAP 2020 surface area and porosity analyser (Micromeritics Instruments Corp.) applying N$_2$ gas at 77 K. Prior to measurement, the samples were degassed for 24 h at 300 °C for pre-treated carbon material and 90 °C for hydride/carbon composite, respectively. Pore size distributions (PSD) were calculated based on a DFT model (NLDFT equilibrium model assuming slit-shaped pores).

Morphological and structural characterization

The morphologies of prepared MgH$_2$/ACF samples were characterised by transmission electron microscopy (TEM) using FEI TITAN 80-300 microscope operating at 200 kV.

Structural properties were characterised by X-ray powder diffraction (XRD) using a Philips X’PERT diffractometer equipped with Cu Ka-radiation, X’Celerator RTMS strip detector and automatic divergence slit. Diffraction data were collected by step scanning with a step size $2\theta = 0.02^\circ$ and a scan step time of 100 s. Powder samples were spread on a silicon single crystal and sealed in the glove box with an airtight hood of Kapton foil. Acquisition and evaluation of the data were done using PANalytical X’PERT Data Collector Ver. 2.1a software and X’PERT HighScore Ver. 2.2 software.

Thermal properties of MgH$_2$/carbon composites

Simultaneous thermogravimetric analysis, differential scanning calorimeter (DSC) and mass spectrometry (TGA-DSC-MS) were conducted in flowing helium (99.999% purity) of 20 ml/min with a heating rate of 5 °C/min using a SETARAM SENSYS Evo thermal analyzer equipped with a GSD 320 mass spectrometer for the analysis of the evolved gas. Calorimetric
measurements were done by means of a HP-DSC 204 NETZSCH high pressure differential scanning calorimeter (DSC) under 3 bar Helium static pressure at different heating rates. Al₂O₃ crucibles with Al₂O₃ lids were used for the measurements. The desorption/absorption and the pressure-composition-isotherm (PCI) measurements were performed under hydrogen using a carefully calibrated modified Sievert’s type apparatus which is described elsewhere[1]. Approximately 1.2 g of sample was used for the measurements. Prior to the PCI measurements, the MgH₂/ACF composite was cycled 3 times by desorption at 350°C under 0.2 bar of initial H₂ pressure and absorption at 300°C under 20 bar of H₂ pressure.

The PCIs for absorption of MgH₂ and the confined nanocomposite were measured at different temperatures by stepwise increasing the hydrogen pressure from 0.5 to 10 bar. The pressure and temperature data were collected at 1 s intervals for 80 000 s for each measurement. The change of H₂ pressure less than 0.02 bar within 20 000 s was chosen as criteria for the real Mg-H equilibrium at each step. The middle-point of plateau corresponding to the hydrogen to meal ratio (H/M) of 1.0 was used as equilibrium pressure for each temperature.

**Figure S2**: BET surface area and total pore volume of ACF and infiltrated MgH₂/ACF composite

**Figure S3**: Pore size distribution of ACF (DFT model)
From the reduced pore volume of carbon scaffold (for pore size in the range from 0.5 to 3 nm) after the treatment of incorporation and the density of MgH$_2$ (1.45 g/cm$^3$), the amount of MgH$_2$ filled into the micro pores was calculated to be 21 mass% in the composite. It was estimated that about 5 % of MgH$_2$ was still on the surface of the carbon material based on the amount of the weight of Bu$_2$Mg precursor added to the ACF in the preparation., which might be the reason for the relatively sharp signals in the XRD patterns for the MgH$_2$/ACF as shown Figure S5

**Calculation of the amount of MgH$_2$ inside the pores**

The micropore volume (pore width < 3 nm) decreased from 0.66 cm$^3$/g (in the empty activated carbon fibre (ACF), before infiltration) to 0.40 cm$^3$/g (in the composite, after infiltration), which corresponds to 0.51 cm$^3$/g for the empty AC.

⇒ *The filled pore volume per 1g of ACF was 0.15 cm$^3$.*

Given a density of 1.45 g/cm$^3$ (MgH$_2$) the filled pore volume corresponds to 1.45 g/cm$^3$ x 0.15 cm$^3$ = 0.21 g of MgH$_2$ per 1 g of ACF.

The total amount of MgH$_2$ per 1 g of ACF was 0.22 g. Hence, 0.22 g − 0.21 g = 0.01 g of the hydride must have stayed outside the pores. This is around 5 % of the hydride.

⇒ *approx. 95 % of the MgH$_2$ in the composite stayed inside the pores.*
TGA with simultaneous DSC was carried out under He flowing at a heating rate of 5 °C/min from 50 to 500 °C. The weight loss prior to the desorption of MgH\textsubscript{2} at 320°C should correspond to the decomposition of residual Bu\textsubscript{2}Mg in the composite, which partly covered the weight loss for MgH\textsubscript{2} in the composite.

![Figure S6. TG-DSC curves for infiltrated MgH\textsubscript{2}/ACF](image)

**Figure S6.** TG-DSC curves for infiltrated MgH\textsubscript{2}/ACF

![Figure S7. DSC curves for infiltrated MgH\textsubscript{2}/ACF and MgH\textsubscript{2} ball milled with ACF](image)

**Figure S7.** DSC curves for infiltrated MgH\textsubscript{2}/ACF and MgH\textsubscript{2} ball milled with ACF

**References:**