Confinement Effects for Lithium Borohydride: Comparing Silica and Carbon Scaffolds

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ABSTRACT: LiBH₄ is a promising material for hydrogen storage and as a solid-state electrolyte for Li ion batteries. Confining LiBH₄ in porous scaffolds improves its hydrogen desorption kinetics, reversibility, and Li⁺ conductivity, but little is known about the influence of the chemical nature of the scaffold. Here, quasielastic neutron scattering and calorimetric measurements were used to study support effects for LiBH₄ confined in nanoporous silica and carbon scaffolds. Pore radii were varied from 8 Å to 20 nm, with increasing confinement effects observed with decreasing pore size. For similar pore sizes, the confinement effects were more pronounced for silica than for carbon scaffolds. The shift in the solid–solid phase transition temperature is much larger in silica than in carbon scaffolds with similar pore sizes. A LiBH₄ layer near the pore walls shows profoundly different phase behavior than crystalline LiBH₄. This layer thickness was 1.94 ± 0.13 nm for the silica and 1.41 ± 0.16 nm for the carbon scaffolds. Quasi-elastic neutron scattering confirmed that the fraction of LiBH₄ with high hydrogen mobility is larger for the silica than for the carbon nanoscaffold. These results clearly show that in addition to the pore size the chemical nature of the scaffold also plays a significant role in determining the hydrogen mobility and interfacial layer thickness in nanoconfined metal hydrides.

1. INTRODUCTION

Lithium borohydride is an ionic compound consisting of Li⁺ cations and [BH₄]⁻ anions, which is of interest for energy storage and conversion.¹–⁶ It contains 18.5 wt % hydrogen and thus is a promising material for solid-state hydrogen storage.¹ However, the hydrogen is released above 673 K in multiple steps, whereas low hydrogen desorption temperatures and fast kinetics are required for integration with low-temperature fuel cells. At room temperature, crystalline LiBH₄ has an orthorhombic structure. This low-temperature phase transforms to a hexagonal phase at about 383 K. Interestingly, Li⁺ ions in the orthorhombic (high temperature) phase of LiBH₄ are highly mobile, resulting in an ionic conductivity of 10⁻² S/cm at 390 K; therefore, this material is also considered to be promising as a solid-state ionic conductor for Li ion batteries.⁵ However, for battery applications, high ionic conductivity at room temperature is required, and it has recently been shown that this might be achieved by partial anion substitution or nanoconfinement.⁵,⁶

It is well known that nanosized materials have physical and chemical properties different from those of the corresponding macrocrystalline materials. The special properties of nanomaterials originate from their high surface to volume ratio.⁷ For metal hydrides, the effects of nanosizing include a reduction of hydrogen diffusion distances and increased specific surface area so that the rate of hydrogen exchange is increased. To sustain the properties of nanoparticles, their growth under operating condition must be avoided, for instance, by confining the hydride nanoparticles in porous materials. These are usually carbon materials because of their chemical inertness and high-temperature stability. Carbon materials are also known to have a high thermal conductivity, which is beneficial for heat management during hydrogen cycling. On the other hand, oxidergous porous materials such as silica are promising for confining LiBH₄ for solid-state battery electrolytes, as low electronic conductivity is a prerequisite for electrolytes in all solid-state batteries.⁵

For LiBH₄, nanoconfinement improves the hydrogen sorption kinetics as well as reversibility. Vajo et al.⁵ reported that nanoconfined LiBH₄ exhibits low activation energy for hydrogen desorption. Upon cycling, the confined phase has a higher hydrogen cycling efficiency than does nonconfined LiBH₄. A study by Cahen et al.⁶ using SBA-15 templated...
ordered porous carbon materials as scaffolds, shows that 
and desorbs about 3 wt % hydrogen within 1.5 h at 573 K, which is only 0.5 wt % for macrocrystalline LiBH4.

Another important effect of nanoconfinement on LiBH4 is the increased \([\text{BH}_4]^−\) and Li⁺ mobility. Ionic conduction reaches 0.1 mS/cm at room temperature for LiBH4 confined in silica materials, more than 3 orders of magnitude higher than for macrocrystalline LiBH4. Nuclear magnetic resonance (NMR) measurements on carbon-confined LiBH4 by Shane et al. showed fast hydrogen mobility for the confined LiBH4. However, the NMR signal also showed two distinct fractions of LiBH4: one with a significantly higher mobility and another with mobility close to that of bulk LiBH4. Quasielastic neutron scattering (QENS) confirmed that LiBH4 confined in carbon scaffolds comprises highly mobile \([\text{BH}_4]^−\) units. It was proposed that this could be related to the strain developed during the confinement procedure. A detailed QENS study by Verdal et al. identified the nature of the motion of the \([\text{BH}_4]^−\) units and showed two fractions of LiBH4 with different mobilities. The mobile fraction increased with decreasing pore size, leading to the proposal of a core—shell model with a mobile shell thickness of about 0.8–0.9 nm at 360 K. Using differential scanning calorimetric (DSC) studies, Liu et al. showed that confinement in carbon pores lowers the solid–solid phase-transition temperature. 

An NMR investigation by Verkuilen et al. was, as far as we are aware, the first to study LiBH4 confined in mesoporous silica instead of carbon. It showed two distinctly different phases; a phase with high Li⁺ and hydrogen mobility and another with Li⁺ and hydrogen mobility that resembles that of macrocrystalline LiBH4.

Herein, we use ordered mesoporous silica and carbon scaffolds to systematically study the impact of pore size, pore geometry, and the chemical nature of scaffolds on confinement effects for nanoconfined LiBH4. By combining hydrogen dynamics studies with calorimetric analysis, we obtain quantitative information on the two different fractions of LiBH4 that exist in the nanocomposites. This study reveals that both the pore size and the nature of the scaffold have a significant influence on the confinement effects. The effects are more pronounced for SiO2 than for carbon materials with similar pore sizes and pore geometry.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation and Characterization. Ordered mesoporous silica, SBA-15, with a 1D pore system was synthesized according to the procedure described by Zhao et al. using block copolymer pluronic P123 as a template and tetraethylorthosilicate as the silica source. Different pore sizes were obtained by changing the aging time and temperature during the hydrothermal treatment (overview in Table 1). The porous carbon materials were carbon aerogels that were synthesized through resorcino-formaldehyde condensation catalyzed by sodium carbonate as described by Pekala et al. The pore size was tuned by changing the organic to water ratio during the gel synthesis.

Before melt infiltration with LiBH4 support porosity was measured with nitrogen physisorption performed at 77 K using a Micromeritics Tristar 3000. The total pore volume was derived from the absorption branch of the nitrogen isotherms at \(p/p_0 = 0.95\). The pore size distributions of the SiO2 were calculated from the desorption branch using the NL-DFT method using the cylindrical pore kernel. The values are derived from the peak of the pore size distribution. Typically for pore sizes <7 nm, the NL-DFT values are more accurate, and about 1 nm larger, than those obtained via the BJH analysis. The pore size distributions of carbon samples were calculated from the desorption branch using the BJH method with the carbon black STSA equation. The surface areas were calculated using the BET equation.

Melt infiltration was employed to confine LiBH4 in the porous scaffolds with loadings corresponding to full pore filling. The details of the melt infiltration procedure have been previously reported. The SiO2 scaffolds were dried prior to sample synthesis under an Ar flow at 473 K for at least 24 h to remove possible residual water. The carbon scaffolds were dried in a hydrogen flow at 873 K for 5 h to remove oxygen-containing groups and to subsequently passivate the resulting dangling bonds with hydrogen as well as to gasify the most reactive fraction of the carbon material.

The preparation of nanocomposites requires good contact between LiBH4 and the scaffolds, and this was achieved by thoroughly mixing them at least for 10 min. After that, the physical mixture was transferred into a graphite sample holder placed in a stainless steel autoclave and initially pressurized to 50 bar of H₂. The pressure is important to prevent partial decomposition during heating. The mixture was heated at 5 K/min to 573 K, which is slightly above the LiBH4 melting temperature, and remained at that temperature for 25 min to allow the melt infiltration of LiBH4 into the pores.

X-ray diffraction patterns of the samples were recorded using a Bruker D8 Advance with Co Kα radiation, \(\lambda = 1.78897 \text{ Å} \).
XRD samples were placed on an airtight sample holder to prevent sample oxidation. Microstructural analysis was performed using an FEI Tecnai 20 transmission electron microscope (TEM) with a field-emission gun operated at 200 kV. The samples were deposited onto carbon holey copper grids (200 mesh) by dipping the grid in a ground powder. Typically, during the insertion of the sample holder into the microscope column, the sample was exposed to air for about 2–5 s.

2.2. Differential Scanning Calorimetry. Differential scanning calorimetric (DSC) measurements were performed with a high-pressure DSC from Mettler Toledo (HP-DSC1). The temperature and the heat flow were calibrated using certified gallium, indium, and zinc references. The nanocomposites (10–20 mg) were placed in a 40 μL hermetically sealed aluminum pan. The data were recorded while heating and cooling between 305 and 565 K at 5 K/min and 20 bar of H2. Each measurement involved two to three cycles to check the sample stability and to verify the reproducibility. The thermograms were processed with STARE software to determine the transition temperatures and the enthalpies. The transition temperature is the extrapolated onset temperature, an intersection of the tangential line drawn through the point of maximum slope and the baseline. The enthalpy is determined from the integration of the phase-transition peak. The enthalpy data of the nanocomposites were compared to those of the macrocrystalline LiBH4 measured under the same conditions. The error in the measured temperature is less than 1º, and that of the measured enthalpy is in the range of 6–8%. To determine the confined fraction of LiBH4, the amount of crystalline, extraporous LiBH4 was measured by comparing the experimental enthalpy of the solid–solid phase transition at the bulk transition temperature for the nanocomposites with that of macrocrystalline LiBH4 measured under the same conditions. The amount of the confined phase is the total amount of LiBH4 in the sample minus the amount of crystalline and hence extraporous LiBH4. When the extraporous LiBH4 peak was not observed, all of the LiBH4 was assumed to be confined.

2.3. Quasielastic Neutron Scattering. Quasielastic neutron scattering (QENS) measurements were carried out using time-of-flight (TOF) neutron spectrometer FOCUS located at continuous spallation source SINQ at the Paul Scherrer Institute, Switzerland.19,20 Isotopically enriched 11B (99.5%) samples (chemical purity 98%), purchased from Katchem, were used to avoid the strong neutron absorption by 10B, present in natural boron. The samples were loaded in lead-sealed, double-walled, hollow cylindrical containers. The diameter of the cylindrical container was 10 mm, and the wall distance (i.e., the sample space) was 1 mm. Incident neutrons were prepared with a wavelength of λi = 4 Å, corresponding to an incident energy of Ei = 5.11 meV and an incident velocity of vi = 989 m/s. The scattering intensity I(2θ, t) is recorded as a function of scattering angle 2θ and time of flight t. Data reduction is carried out using data analysis and visualization environment DAVE21 to convert the instrument-specific I(2θ, t) to the scattering function S(Q, ω). Thereby, the scattering intensity is expressed as a function of the momentum transfer hQ = hki − hko, where ki and k0 are the incident and scattering wave vectors, and as a function of the energy transfer hω = Ei − Ef, where Ef and Ei are the incident and scattering neutron energies, respectively. Because of the large incoherent scattering cross section σincoh of hydrogen as compared to those of lithium, carbon, and boron, we attribute all scattering intensity to the incoherent scattering of hydrogen. Hence, the contributions of other species, coherent scattering, and multiphonon events are neglected. In bulk LiBH4, rapid reorientations of the [BH4]− anions are responsible for the quasi-elastic signal. At the instrumental settings used, the energy resolution defining the width of the elastic line equals ΔE = 0.2 meV. Data acquisition and treatment were carried out as described earlier, and the spectra were binned in a range of Q values of 0.5 Å−1 < Q < 2.5 Å−1. The resulting QENS spectra were analyzed using general purpose curve-fitting utility PAN, following the procedure described in the previous publication.10

3. RESULTS AND DISCUSSION

3.1. Structural Properties. Table 1 gives an overview of the textural properties of the supports as well as the properties of the nanocomposites, including the loading and the amount of confined LiBH4 in each sample, i.e., the fraction of pores that was filled. We tuned the pore radii from 3.3 to 6.1 nm and from 3.1 to 20 nm for the silica and carbon materials, respectively. The ordered mesoporous silica SBA-15 materials comprise uniform parallel pores connected by intrawall porosity. The porosity of the carbon materials originates from interparticle space and is dominated by carbon particles connected by intrawall porosity. As confirmed by the transmission electron micrographs of these supports (Figure S1). The pore volumes of the supports are between 0.3 and 0.8 cm3/g for silica materials and between 0.53 and 1.37 cm3/g for the carbon scaffolds, and this enables us to make samples with confined LiBH4 loading ranging from 13.2 to 36 wt % with 60–100% pore volumes filled with LiBH4. The high carbon pore filling (>70%) is achieved by the proper mixing of LiBH4 and the scaffolds by multiple melt infiltration (at least two sessions of melting and cooling under hydrogen pressure).

3.2. Size- and Interface-Dependent Hydrogen Dynamics. Neutron scattering is a powerful tool to study the dynamics of complex hydrides because of the incoherent neutron scattering cross-section of hydrogen. Therefore, the effects of pore size and the nature of the scaffold on the hydrogen dynamics of our nanoconfined LiBH4 were investigated using QENS. QENS probes the transfer of small amounts of energy compared to the neutron incident energy. These small energy transfers are caused by energy redistributions in the samples originating from atomic translations or rotations. The QENS spectra of the macrocrystalline (bulk) LiBH4 recorded between 300 and 500 K (Figure 1A) show that the patterns changed significantly above 380 K. This is a clear indication of the structural phase transition of LiBH4 at this temperature. The low-temperature phase is characterized by a broad inelastic feature with distinct structure at around 1.5 ms. The elastic line is clearly separated from the inelastic part of the spectrum by an intensity minimum, indicative of a low density of states at low energy transfers. Above the phase-transition temperature, the separation between the elastic and inelastic parts of the spectrum disappears and the inelastic part of the spectrum shows no distinct features. In the HT phase, the quasielastic component, seen as a broad background around the elastic line, broadens, and the intensity at the base of the elastic line drops with increasing temperature (with the arrow in Figure 1 pointing to this feature).

Figure 1B,C shows the time-of-flight patterns for LiBH4 confined in carbon and silica (SBA-15) scaffolds with pore radii of 5.6 and 5.9 nm, respectively. Compared to macrocrystalline LiBH4, the broadening of the base of the elastic line is less pronounced. Also, the sudden shift of the spectra with
temperature, representative of the structural phase transition, is less apparent for the nanoconfined LiBH₄, in line with previous results based on NMR. These results are also in line with previous QENS measurements that showed that the structural phase transition of LiBH₄ was significantly suppressed when the compound was confined in high-surface-area nanoporous graphite (HSAG) with an average pore size of between 2 and 3 nm.¹⁰

Even though, comparing the silica and carbon materials, the spectra look rather similar at first glance, small but distinct differences are present. In the case of the silica (Figure 1C), all high-temperature spectra coincide at the base of the elastic line. In contrast, for the carbon case (Figure 1B) there is a clear temperature dependence of the quasielastic broadening, although it is less pronounced than for macrocrystalline LiBH₄ (Figure 1A). Therefore, LiBH₄ confined in carbon displays intermediate behavior between macrocrystalline LiBH₄ and LiBH₄ confined in SiO₂. Because the materials have very similar pore sizes, we can conclude from these observations that silica materials exert stronger confinement effects on LiBH₄ than do carbon scaffolds.

The QENS results suggest the presence of at least two distinct fractions of LiBH₄ in the silica scaffold; however, the present data do not allow us to unambiguously deconvolute the measured QENS spectra into two Lorentzian contributions. Hence, we modeled the spectra using an elastic peak of width Γₑ and an integrated area Iₑ and a single Lorentzian curve with a width Γₚₑ and an integrated area Iₚₑ for the quasi-elastic

Figure 1. Time-of-flight spectra for bulk LiBH₄ (A) and LiBH₄ confined in carbon (B) and SiO₂ (C) with pore radii of 5.6 and 5.9 nm, respectively.

Figure 2A–C shows the time-of-flight spectra of a series of LiBH₄/SiO₂ nanocomposites with different pore sizes. A close look at the spectra reveals that at high temperatures the signature of macrocrystalline LiBH₄ is less pronounced for the smaller pore radii. The temperature at which the signature of the structural phase transition disappears decreases with decreasing SiO₂ pore size: the TOF spectrum of SiO₂-5.9 shows the signature of the high-temperature phase at ≥380 K, whereas for SiO₂-4.4 and SiO₂-3.6, the highest temperatures at which it is observed are 350 and 333 K, respectively. This means that the temperature at which the structural transition for nanoconfined LiBH₄ occurs decreases with decreasing pore radius. Hence, the hydrogen dynamics of nanoconfined LiBH₄ are also influenced by the pore size of the silica scaffold material.

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broadening. The width $\Gamma_{el}$ of the elastic line was fixed to the width of the measured elastic line of a vanadium standard sample, corresponding to the instrumental resolution.

In macrocrystalline LiBH$_4$, the phase transition is evidenced by a sudden change in the quasielastic broadening and a distinct change in activation energy between 360 and 390 K. All quasielastic broadenings measured on the confined samples lie in between the data for macrocrystalline LiBH$_4$. With decreasing pore size, the values deviate more and more from the bulk values. The deviation from the bulk behavior is larger for the carbon in the HT phase, whereas for the SiO$_2$ it is larger in the values. The deviation from the bulk behavior is larger for the pore size, the values deviate more and more from the bulk behavior at room temperature. At low temperature, $\Gamma_{el}$ increases with decreasing pore size, indicative of increasing mobility due to confinement. The hydrogen mobility at low temperatures in the confined samples is much higher than for macrocrystalline LiBH$_4$, and the smaller the pore sizes, the stronger the deviation from the bulk value.

Figure 3. Temperature dependence of the quasielastic broadening for macrocrystalline LiBH$_4$ and LiBH$_4$ confined in SiO$_2$ and carbon with different pore sizes.

3.3. Impact of Confinement on the Phase-Transition Temperature. The hydrogen mobility as measured by quasielastic neutron scattering shows clear differences between LiBH$_4$ nanocarbons in SiO$_2$ and in C matrices, indicating that the confinement effects are influenced by the chemical nature of the scaffold. A quantifiable aspect of confinement is the change in the thermodynamic stability and hence the phase-transition temperatures and enthalpies. Because the LiBH$_4$ phase transitions involve a significant amount of enthalpy, calorimetry is a powerful tool for investigating the phase-transition processes. Figure 4 illustrates DSC measurements of macrocrystalline LiBH$_4$ and LiBH$_4$ confined in 3.1 nm pores of a carbon matrix. During heating, the low-temperature solid phase transforms into a high-temperature phase with an onsets temperature of 386 K for the macrocrystalline LiBH$_4$. Further heating leads to the melting at 558 K. During cooling, liquid LiBH$_4$ starts to solidify at a slightly lower temperature than for melting.

For the confined LiBH$_4$, the DSC shows two additional peaks; one below the solid–solid phase transition and the other below the melting temperature. If all LiBH$_4$ is confined in the pores, then only the depressed peaks belonging to the confined phase were observed, as shown for some of the nanoconfined samples (e.g., samples SiO$_2$-4.4 and C-3.8) in Figures 5A and 6A. The peaks of the confined phase are broadened, and the intensity of the peaks corresponding to features of the bulk is reduced. Another important point we found with DSC is that the phase transitions are fully reversible under hydrogen pressure; we found no indication of side reactions with either the carbon or the silica scaffolds. Table 2 gives an overview of the calorimetric results for LiBH$_4$ confined in silica and carbon materials with different pore sizes. The table lists the onset temperatures, the depression in the phase transition, and the enthalpies of the solid–solid phase transition and melting. The onset temperatures and the enthalpies depend on the pore radius. The melting temperature is shifted more than 100° down for LiBH$_4$ confined in 3.3 nm SiO$_2$ pores.

The DSC thermograms of melting behavior of LiBH$_4$/SiO$_2$ and LiBH$_4$/C are shown in Figure 5A. The size dependence of the melting temperatures was analyzed by plotting $\Delta T$ as a function of $1/r$, as shown in Figure 5B. It can be seen that the melting-point depression is inversely proportional to the pore radius of both the SiO$_2$ and C scaffolds.

It is generally accepted that a shift in melting temperature is related to size and interface effects, and it is typically ascribed to the increasing contribution of interfacial energy with decreasing size. The relationship between the depressed melting temperature and the particle radius is often described by the Gibbs–Thomson relation, i.e., eq 1, where the ratio between the depressed temperature ($\Delta T$) and the temperature of the bulk LiBH$_4$ ($T_0$) scales with the interface energy ($\Delta y$) and inverse pore radius ($r_p$).

$$\frac{\Delta T}{T_0} = \frac{2\Delta y V_m}{\Delta H(t_p - t)} \tag{1}$$

In eq 1, the enthalpy of the phase transition, $\Delta H_i$ is assumed to be independent of the particle size. This simplified description also assumes that the molar volume, $V_m$, is the same for both phases involved in the transition. In some cases, the application of the Gibbs–Thomson relation requires a correction for an interfacial layer thickness, $t$, a fraction of the material that does not participate in the phase transition. For example, for ice melting in nanopores the layer thickness is on the order of 0.4 nm. To estimate interface energies from our experimental data, the observed temperature depressions were fitted using eq 1. Assuming no inert interfacial layer ($t = 0$), the resulting
interface energy is 0.018 J/m². If including an inert layer, the surface energy is 0.015 J/m² and \( t \) is 0.6 nm. This gives a first indication of the interfacial energy, but we show in the next section how the interfacial energy can be determined more accurately. It is interesting to observe that the calculated effective interfacial energy for the confined samples is about an order of magnitude lower than the surface energy of macrocrystalline LiBH₄, \( \sim 0.12 \) J/m².²⁹,³⁰ This points to a strong favorable interaction between the silica pore walls and the nanoconfined LiBH₄ resulting in a much lower effective interfacial energy and hence a high stability of the confined LiBH₄.

The impact of the size on the solid–solid phase-transition temperatures has never been investigated in detail, especially for silica scaffolds; hence, we did a detailed study on these effects for the carbon and silica materials. For LiBH₄ confined in silica, the depression is largest for the smallest pore radius and up to 49° for SiO₂ with 3.3 nm pores (Figure 6A, upper frame). As can be seen in Figure 6A (lower frame), for carbon scaffolds the impact of pore size on the solid–solid depression is much smaller than for the silica scaffolds. For example, the depression was 49 K for SiO₂-3.3 and only 27 K for C-3.1 even though they have similar pore radii. The differences are clearly seen in Figure 6B in which the phase-transition temperature shifts are plotted as a function of \( 1/r \).

### 3.4. Comparing Silica and Carbon Scaffolds.

In all cases, the measured enthalpy of the solid–solid phase transition of the confined phase (Table 2) decreases with decreasing pore size of the scaffold. Decreasing transition enthalpies of confined phases have also been observed for water,²¹ organic materials,²² and
metals. Figure 7a shows the measured enthalpies normalized to that of the macrocrystalline LiBH$_4$. If we assume a core–shell model such as that proposed by Verdal et al., namely, that the measured enthalpy is due to material in the core of the pores that undergoes a phase transition (and hence material close to the pore wall does not contribute) and cylindrical pore geometries, then the relative enthalpy dependence on the pore radius ($r_p$) can be expressed by eq 2, where $t$ is the interfacial thickness.

$$\frac{\Delta H_{\text{confined}}}{\Delta H_{\text{bulk}}} = \left(1 - \frac{t}{r_p}\right)^2$$

(2)

Fitting the data using eq 2 results in an interfacial layer thicknesses of 1.41 ± 0.16 and 1.94 ± 0.13 nm for the carbon and silica scaffolds, respectively. For carbon-confined LiBH$_4$, the value is larger than the 0.83–0.99 nm at 373 K estimated by Shane et al. The thicker interfacial layer for LiBH$_4$/SiO$_2$ indicates that the specific interaction of LiBH$_4$ with SiO$_2$ extends over longer distances than for C. It is important to mention here that pore walls are not atomically flat. For instance, it is known from the work of Gommes et al. that the amplitude of surface corrugation of the silica (SBA 15) is 1.6 nm, which is close to the value of 1.94 nm observed for the LiBH$_4$ interfacial layer. However, the specific surface area of carbon materials and hence the effective pore corrugation are even larger than those for silica with a similar pore size (Table 1). This strengthens the conclusion that the confinement effects inherently extend over longer distances in the case of silica than for carbon, as the difference in interfacial layer thickness cannot be attributed to pore corrugation effects.

Using those interfacial layer thicknesses determined from the above analysis, the effective interfacial energy differences for the two structural phases of LiBH$_4$ confined in either SiO$_2$ or C can accurately be determined and are summarized in Table 3. The interfacial energy difference for the SiO$_2$/LiBH$_4$ interface (0.053 J/m$^2$) is higher than for the C/LiBH$_4$ interface (0.033 J/m$^2$). This is most likely due to the different interaction between LiBH$_4$ and the pore walls of the scaffold materials. The surface of silica is polar with a surface energy of about 0.260 J/m$^2$, whereas the carbon surface is apolar with a low surface energy of 0.032 J/m$^2$, and hence a stronger interaction with silica than with carbon might be expected.

**3.5. Comparing Carbon Scaffolds with Different Pore Size Distributions.** Carbon aerogels have a broader pore size distribution than the ordered mesoporous silica (SBA-15). We therefore additionally measured the calorimetric properties of LiBH$_4$ confined in ordered nanoporous carbon scaffolds possessing relatively narrow pore size distributions (Figure S3) to investigate whether the carbon pore structure and pore size distributions have a large influence on the confinement effects. Figure 8 shows the DSC thermograms of nano-composites prepared with microporous carbon (~0.8 nm pore radius), CMK-3 (~1.8 nm pore radius), and Kroll carbons (ca. 4.9 nm pore radius). For comparison, the thermograms of nanocomposites prepared with carbon aerogel and SiO$_2$ (~4.8 nm pore radius) are added for comparison. The asterisk (*) indicates the onset temperature of the phase transition for the nanocomposed fractions.
Table 4. Summary of the Properties and DSC Results for LiBH₄ Confined in Ordered Nanoporous Carbon Scaffolds

| sample | LiBH₄/wt % | fraction confined/% | $T_{\text{onset, mhd-nhd}}$/K | $\Delta T_{\text{mhd-nhd}}$/K | $T_{\text{peak}}$ | $\Delta H_{\text{mhd-nhd}}$/kJ/mol | t/nm |
|--------|------------|---------------------|-----------------------------|-----------------------------|----------------|---------------------------------|------|
| C₉₀.₈  | 30.8       | 82                  | 301                         | 77                          | 340            | 0.36                           | 1.30 |
| C₉₁.₈  | 49.2       | 84                  | 292                         | 86                          | 376            | 2.3                            | 1.27 |
| C₉₄.₉  | 63.5       | 97                  | 292                         | 86                          | 376            | 2.3                            | 1.27 |

and 6.1 nm pore radii, respectively) are also included. Interestingly, only the peak corresponding to the structural phase transition for the unconfined (macroporous) LiBH₄ is observed in sample C₉₀.₈ (prepared with microporous carbon). Note that about 82% of the LiBH₄ in this sample is confined (Table 4). We attribute the absence of the structural phase transition for the confined fraction to the fact that the pore radius is below the interfacial layer thickness (1.41 ± 0.16 nm) determined for LiBH₄ nanoconfined in carbon materials. Therefore, LiBH₄ confined in carbon pores below this range is not expected to show any phase transition.

The onset temperatures for the structural phase transition for the confined fraction of LiBH₄ in C₉₁.₈ and C₉₄.₉ are 301 and 292 K, respectively, compared to about 378 K for macroporous LiBH₄. The slightly lower onset phase-transition temperature for C₉₄.₉ is due to the presence of carbon with pores of less than 1.8 nm in radius. This also explains why the phase transition extends over a longer temperature range than that of C₉₁.₈. However, the peak of the phase transition is clearly at a much higher temperature for C₉₄.₉ than for C₉₁.₈. These observations indicate that the pore size distributions of the scaffold are reflected in the peak width (broadness of the phase-transition event) whereas the average pore size of the scaffold determines the peak temperature of the phase transition. A clear proof of this is the fact that the DSC profile of C₉₄.₉ is similar to that of the nanocomposite prepared with carbon aerogel with a similar average pore size (C₉₄.₉) and pore-size distributions but is much sharper because of the slight differences in pore size distributions (Figure S3). On the other hand, the peak temperatures for C₉₁.₈ and C₉₄.₉ are at even a slightly higher temperature than for SiO₂-6.1 despite the fact that this silica has larger pores. These results confirm that the confinement effects are indeed more pronounced for SiO₂ than for carbon. Another clear evidence comes from the fact that the nanocomposites prepared with the ordered mesoporous carbon materials have interfacial layer thicknesses (Table 4) that are very close to the average value determined for the samples prepared with carbon aerogel (Table 1). The interfacial layer thickness for these samples is estimated from eq 2. The observed difference in the nanococondensation effects is mainly due to the differences in the surface chemistry of the nanoscaffolds. Geometric differences might also play a role; SBA-15 has a more defined pore geometry (hexagonally packed cylindrical pores) than the ordered nanoporous carbon.

4. CONCLUSIONS

Quasielastic neutron scattering shows a clear impact of confinement on the hydrogen mobility, with the behavior of LiBH₄ in carbon scaffolds being closer to that of macroporous LiBH₄ than when confining LiBH₄ in silica scaffolds. The temperature of the solid—solid phase transition of LiBH₄ is also depressed more strongly for silica than for carbon scaffolds and shifts from 387 to 338 K for LiBH₄ confined in 3.3 nm silica pores. Pore-size-dependent enthalpy measurements confirm that there is a significant fraction of LiBH₄ near the pore walls that does not undergo a structural phase transition, and assuming that this is a well-defined interfacial layer, we quantify its thickness as 1.94 ± 0.13 nm for SiO₂ and 1.41 ± 0.16 nm for carbon scaffolds. If interpreting the shift of the phase transition in terms of the interfacial energy difference, the difference between the orthorhombic- and hexagonal-phase LiBH₄-SiO₂ interfaces is 0.053 J/m², whereas for the LiBH₄—carbon interfaces this is only 0.033 J/m². Hence, we show a size dependence of the hydrogen dynamics and confinement energetics of LiBH₄ on pore size as well as on the chemical nature of the scaffolds. This suggests that the nature of the scaffold and surface modification are important tools for tuning the hydrogen sorption and ion conduction properties of confined complex hydrides.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b13094.

Detailed preparation method for ordered nanoporous carbon, transmission electron micrographs, and pore size distribution of silica and carbon scaffolds. (PDF)

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Notes

The authors declare no competing financial interest.

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