Supporting Information:

On the Nature of Interface Interactions Leading to High Ionic Conductivity in LiBH$_4$/SiO$_2$ Nanocomposites

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1 Synthesis protocols

1.1 Mesoporous silica scaffolds

**SBA-15** The primary mesopore diameter of Santa Barbara Amorphous-15\(^{51}\) (SBA-15) can be varied by tuning the hydrothermal synthesis temperature.\(^{52}\) A mixture of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123), hydrochloric acid (37\%) and water was dissolved at 35°C. Tetraethyl orthosilicate (TEOS) was added dropwise and the mixture was stirred at 40°C for 24 h. The molar ratios were 0.015:5.2:147:1 for P123:HCl:H\(_2\)O:TEOS respectively. Hydrothermal treatment was done by heating the mixture to 40, 70, 85, 100 or 120°C in a closed bottle or autoclave for 44 h, after which the solid precipitate was washed with water. The product was dried, ground, and subsequently calcined in air by increasing the temperature to 550°C with a ramp of 1.2°C/min and kept at this temperature for 12 h. The silicas are referred to as SBA-15 followed by their hydrothermal treatment temperature.

**MCM-41** The pore diameter of Mobil Composition of Matter 41\(^{53}\) (MCM-41) was tuned by the choice of surfactant. Synthesis was performed as described by Cheng et al.\(^{54}\) Thick-walled MCM-41 was synthesized by using elevated hydrothermal treatment temperatures (170-180°C).\(^{55}\) A mixture of water, n-alkyl-trimethylammonium bromide (C\(_n\)TAB, n=10,14,16) and tetramethyllammonium hydroxide (TMAOH, 25\%) was dissolved at 30°C. Aerosil was added and the mixture was stirred for 2 h, then left standing at 30°C for 20 h. The molar ratios in the mixture were 39:0.26:0.18:1 for H\(_2\)O:C\(_n\)TAB:TMAOH:SiO\(_2\) respectively. Hydrothermal treatment was done by heating the mixture to 150, 170 or 180°C in an autoclave for 44 h. The MCM-41 was subsequently washed and calcined as described for SBA-15. The silicas are referred to as MCM-41 followed by the C\(_n\)(TAB) chain length and the hydrothermal treatment temperature; the suffix ‘-2’ is used to differentiate scaffolds prepared using the same procedure.

1.2 LiBH\(_4\)/SiO\(_2\) nanocomposites

All silica scaffolds were dried at 300°C in a glass reactor under a constant flow of inert gas, using a ramp of 5°C/min, and kept at that temperature for 6 h. Subsequently, the dried silica was stored in gloveboxes with H\(_2\)O and O\(_2\) levels typically ≤ 1 ppm.

The LiBH\(_4\)/SiO\(_2\) nanocomposites were prepared via melt-infiltration of the dried silica scaffolds.\(^{56}\) LiBH\(_4\) (95\%, Sigma-Aldrich) and dried silica were hand-mixed in the glovebox. The LiBH\(_4\) loadings (fraction of pores that would be filled with LiBH\(_4\) if all LiBH\(_4\) infiltrates) can be found in tables S2 and S3 for the samples used for impedance spectroscopy and NMR experiments respectively. These mixtures were transferred to borosilicate glass vials and placed in a stainless-steel autoclave. Approximately 50 bar H\(_2\) gas was applied and the autoclave was heated to 300°C using a ramp of 3°C/min, and kept at this temperature for 30 min. After cooling down, the H\(_2\) pressure was released and the samples were transferred into the glovebox without exposure to air. Nanocomposites used for studies by NMR are named by their scaffold suffixed by \(^i\) or \(^{ii}\) to distinguish nanocomposites of different batches that use the same silica scaffold.
Table S1: Structural properties of the silica scaffolds.

| Silica ID     | \(S_{\text{BET}}\)^a  | \(V_{\text{total}}\)^b | \(V_{\text{pore,meso}}\)^c | \(V_{\text{pore,micro}}\)^c | \(d_{\text{BJH}}\)^d | \(d_{\text{DFT}}\)^e | \(t_{\text{BJH}}^{(100)}\) | \(t_{\text{DFT}}^{(100)}\) | \(t_{\text{BJH}}^{(200)}\) | \(t_{\text{DFT}}^{(200)}\) |
|--------------|-----------------|-----------------|-----------------|-----------------|---------------|---------------|---------------|---------------|---------------|---------------|
| SBA-15-40    | 682 0.54        | 0.35 (65)       | 0.17 (31)       | 5.6             | 7.1           | 3.2           | 1.7           | 3.8           | 2.3           |
| SBA-15-70    | 735 0.77        | 0.51 (67)       | 0.15 (19)       | 6.6             | 8.3           | 2.7           | 1.0           | 3.4           | 1.7           |
| SBA-15-85    | 793 0.83        | 0.51 (62)       | 0.21 (25)       | 7.2             | 9.2           | 2.4           | 0.4           | 3.0           | 1.0           |
| SBA-15-100   | 724 1.03        | 0.73 (71)       | 0.10 (10)       | 8.9             | 11.2          | 1.1           | -1.2          | 1.7           | -0.6          |
| SBA-15-120   | 491 0.96        | 0.63 (66)       | 0.09 (9)        | 10.1            | 12.7          | -             | -             | 0.7           | -1.9          |
| MCM-41-C10-150 | 845 0.69    | 0.44 (63)       | 0.00 (0)        | 1.9             | 3.0           | 2.3           | 1.2           | 2.5           | 1.4           |
| MCM-41-C14-150 | 979 0.86   | 0.78 (91)       | 0.00 (0)        | 2.7             | 4.0           | 1.9           | 0.6           | 1.9           | 0.6           |
| MCM-41-C16-140 | 1113 1.13  | 0.93 (83)       | 0.00 (0)        | 2.9             | 4.2           | 1.6           | 0.3           | 1.7           | 0.4           |
| MCM-41-C16-150 | 1083 1.04  | 0.96 (92)       | 0.00 (0)        | 3.1             | 4.5           | 1.7           | 0.3           | 1.8           | 0.4           |
| MCM-41-C16-165 | 550 0.55   | 0.40 (73)       | 0.07 (13)       | 3.9             | 5.3           | 2.1           | 0.7           | 3.2           | 1.8           |
| MCM-41-C16-170 | 474 0.46  | 0.33 (72)       | 0.06 (13)       | 3.7             | 5.1           | 2.3           | 0.9           | 2.5           | 1.1           |
| MCM-41-C16-180 | 346 0.36  | 0.33 (91)       | 0.00 (0)        | 3.3             | 4.6           | 2.9           | 1.6           | 3.3           | 2.0           |
| MCM-41-C16-150-2 | 1194 1.20 | 1.06 (88)       | 0.00 (0)        | 3.2             | 4.5           | 1.7           | 0.4           | 1.8           | 0.5           |
| MCM-41-C16-165-2 | 564 0.59  | 0.42 (72)       | 0.08 (13)       | 3.7             | 5.2           | 2.4           | 0.9           | 2.7           | 1.2           |
| MCM-41-C16-180-2 | 421 0.44  | 0.36 (83)       | 0.03 (6)        | 3.3             | 4.7           | 3.0           | 1.6           | 3.3           | 1.9           |
| Aerosil 90   | 71 0.18        | -               | -               | 0.02 (12)       | -             | -             | -             | -             | -             |
| Aerosil 300  | 278 0.89       | -               | -               | 0.04 (5)        | -             | -             | -             | -             | -             |
| Aerosil 380  | 352 1.06       | -               | -               | 0.05 (4)        | -             | -             | -             | -             | -             |

\(a\) Specific surface area via the BET method.\(^{57}\) (N\(_{2}\)-physisorption)
\(b\) Total volume of pores at 0.997 P/P\(_0\). (N\(_{2}\)-physisorption)
\(c\) Pore volumes determined using the t-plot method and the Harkins-Jura reference isotherm.\(^{58}\) (N\(_{2}\)-physisorption)
\(d\) Pore diameter via the classical BJH method on the adsorption isotherm.\(^{59}\) (N\(_{2}\)-physisorption)
\(e\) Pore diameter via density functional theory fit.\(^{510}\) (N\(_{2}\)-physisorption)
\(f\) The thickness \(t\) of the pore walls of MCM-41 and SBA-15 was obtained by relating the lattice spacing \(a_0\) (XRD, (100) or (200) reflection) with the pore diameter \(d_{\text{pore}}\) (N\(_{2}\)-physisorption, DFT or BJH model) via \(t = a_0 - d_{\text{pore}}\), where \(a_0\) was obtained from XRD via \(a_0 = 2d_{000}/\sqrt{3}\) (n=1 or 2).\(^{511}\) For SBA-15, the DFT model for cylindrical pores is less applicable, resulting in negative thickness values.
Table S2: Properties and ionic conductivity of the LiBH$_4$/SiO$_2$ nanocomposites used for conductivity measurements.

| Silica ID      | Loading (wt%)$^a$ | Confined (%$V_p$$^b$) (%)$^c$ | Conduct. (µS/cm)$^d$ | $E_{act}$ (eV)$^e$ | Fig. 1 | Pressure (MPa)$^g$ |
|----------------|-------------------|-------------------------------|---------------------|-------------------|--------|-------------------|
| SBA-15-40      | 32                | 134                           | 82                  | 7.1               | 0.51   | ✓                 |
| SBA-15-70      | 36                | 128                           | 79                  | 1.1               | 0.58   | ✓                 |
| SBA-15-85      | 38                | 128                           | 73                  | 6.5               | 0.58   | ✓                 |
| SBA-15-100     | 41                | 126                           | 64                  | 9.0               | 0.54   | ✓                 |
| SBA-15-120     | 37                | 123                           | 76                  | 5.6               | 0.52   | ✓                 |
| MCM-41-C$_{14}$-150 | 40        | 130                           | 63                  | 9.6               | 0.48   | ✓                 |
| MCM-41-C$_{16}$-140 | 44           | 129                           | 50                  | 17.1              | 0.48   | ✓                 |
| MCM-41-C$_{16}$-150 | 45        | 130                           | 73                  | 11.0              | 0.45   | ✓                 |
| MCM-41-C$_{16}$-150 | 52        | 169                           | 64                  | 17.6              | 0.46   | ✓                 |
| MCM-41-C$_{16}$-150 | 59        | 204                           | 86                  | 8.8               | 0.49   | ✓                 |
| MCM-41-C$_{16}$-150 | 62        | 226                           | 63                  | 7.4               | 0.51   | ✓                 |
| MCM-41-C$_{16}$-165 | 29        | 131                           | 81                  | 3.9               | 0.52   | ✓                 |
| MCM-41-C$_{16}$-165 | 46        | 251                           | 77                  | 7.1               | 0.50   | ✓                 |
| MCM-41-C$_{16}$-180 | 31        | 208                           | 88                  | 1.6               | 0.49   | ✓                 |
| MCM-41-C$_{16}$-150 | 59        | 204                           | 86                  | 0.8               | 0.65   | 75                |
| MCM-41-C$_{16}$-150 | 55        | 175                           | 68                  | 7.0               | 0.50   | 75                |
| MCM-41-C$_{16}$-150 | 46        | 251                           | 77                  | 0.6               | 0.62   | 75                |
| MCM-41-C$_{16}$-165 | 37        | 175                           | 86                  | 1.9               | 0.56   | 75                |
| MCM-41-C$_{16}$-165 | 40        | 204                           | 99                  | 2.8               | 0.50   | 75                |
| MCM-41-C$_{16}$-170 | 28        | 151                           | 115                 | 1.3               | 0.53   | 75                |
| MCM-41-C$_{16}$-180 | 34        | 200                           | 100                 | 0.2               | 0.61   | 75                |
| Aerosil 90     | 44                | -                             | 0%$^h$              | 1.0               | 0.58   | ✓                 |
| Aerosil 300    | 44                | -                             | 18%$^h$             | 4.5               | 0.57   | ✓                 |
| Aerosil 380    | 44                | -                             | 47%$^h$             | 2.0               | 0.55   | ✓                 |

$^a$ Mass percentage of LiBH$_4$ in the nanocomposite.

$^b$ Theoretical fraction of silica pores filled with LiBH$_4$.

$^c$ Fraction of silica pores filled with LiBH$_4$ according to DSC.

$^d$ Ionic conductivity at 30 °C, interpolated from a linear fit of the Arrhenius plot between ambient temperature and 100 °C (figure S5).

$^e$ Apparent activation energy of the Li-ion hopping process, determined from a linear fit of the Arrhenius plot between ambient temperature and 100 °C (figure S5).

$^f$ A checkmark indicates whether the nanocomposite was included in Figure 1. Nanocomposites with excessive LiBH$_4$ loadings, thick walls (compression differences, see figure S17) or different pressures were excluded from this figure.

$^g$ The pressure for making the pellet consisting of lithium foil|nanocomposite|lithium foil, which was subsequently used in impedance spectroscopy.

$^h$ Fumed silica lacks a well-defined pore structure. Hence, the fraction of LiBH$_4$ that does no longer undergo the bulk phase transition around 110 °C is shown instead.
Table S3: Composition of the nanocomposites used in the studies with NMR. A suffix i or ii is added to the silica scaffold ID to distinguish two nanocomposites that use the same silica scaffold.

| Nanocomposite | Loading | Confined | Dynamic LiBH$_4$ |
|---------------|---------|----------|-----------------|
| Silica ID + i/ii | (wt%)$^a$ | (%$\nu_p$)$^b$ | (%)$^c$ | (%)$^d$ |
| SBA-15-40$^i$ | 24 | 92 | 85 | 36 |
| SBA-15-40$^{ii}$ | 24 | 90 | 86 | 27 |
| SBA-15-85$^i$ | 30 | 91 | 75 | 19 |
| SBA-15-85$^{ii}$ | 30 | 90 | 81 | 27 |
| SBA-15-120$^i$ | 30 | 87 | 70 | 21 |
| SBA-15-120$^{ii}$ | 30 | 87 | 70 | 17 |
| MCM-41-C$_{10}$-150$^i$ | 21 | 90 | 37 | 19 |
| MCM-41-C$_{10}$-150$^{ii}$ | 21 | 90 | 43 | 21 |
| MCM-41-C$_{14}$-150$^i$ | 32 | 96 | 59 | 20 |
| MCM-41-C$_{14}$-150$^{ii}$ | 32 | 95 | 64 | 19 |
| MCM-41-C$_{16}$-150$^i$ | 37 | 90 | 68 | 13 |
| MCM-41-C$_{16}$-150-2$^i$ | 39 | 90 | 59 | 13 |
| MCM-41-C$_{16}$-170$^i$ | 19 | 91 | 82 | 33 |
| MCM-41-C$_{16}$-180$^i$ | 17 | 93 | 91 | 53 |
| MCM-41-C$_{16}$-180-2$^i$ | 19 | 91 | 79 | 43 |
| Aerosil 90$^i$ | 11 | - | 40%$^e$ | 3 |
| Aerosil 300$^i$ | 29 | - | 66%$^e$ | 4 |
| Aerosil 300$^{ii}$ | 35 | - | 74%$^e$ | 3 |

$^a$ Mass percentage of LiBH$_4$ in the nanocomposite.
$^b$ Theoretical fraction of silica pores filled with LiBH$_4$.
$^c$ Fraction of silica pores filled with LiBH$_4$ according to DSC.
$^d$ Fraction of LiBH$_4$ in the most-dynamic fraction at 30 °C as determined via static $^1$H NMR spectra (figure S6). The error is 4 percent point or less.
$^e$ Fumed silica lacks a well-defined pore structure. Hence, the fraction of LiBH$_4$ that does no longer undergo the bulk phase transition around 110 °C is shown instead.
Figure S1: N$_2$-physisorption isotherms of the silicas. Adsorption isotherms are shown in red, desorption isotherms in blue. An arbitrary offset was applied for clarity.
Figure S2: Pore size distributions of the silicas according to the classical BJH model\(^{89}\) applied to the adsorption isotherm (figure S1).
Figure S3: Normalized low angle powder X-ray diffraction patterns of the silica scaffolds. The major peaks of MCM-41 and SBA-15 correspond, from left to right, to the (100), (110) and (200) reflections, respectively. Higher reflections are visible for some silica scaffolds. Aerosil has no long-range ordering and is hence featureless. An arbitrary offset was applied for clarity. The sloping baseline on the left is an artifact due to direct beam exposure.
Figure S4: Transmission electron micrographs of (a) MCM-41-C$_{16}$-150 and (b) MCM-41-C$_{16}$-180, showing the ordered porous structure of both silica scaffolds. Mesoporous silica scaffolds are very prone to electron beam damage$^{31}$, hence different maximum zoom levels were used. Some beam damage is visible in b).
Figure S5: Arrhenius plots of the ionic conductivities of nanocomposites using (a) SBA-15, (b) MCM-41 and (c) fumed silica (Aerosil) scaffolds as function of temperature, as shown in figure 1 and listed in table S2.
Figure S6: Normalized $^1$H NMR spectra of nanocomposites, measured at a field of 7.05 T.
Figure S7: Normalized $^7$Li solid echo NMR spectra of nanocomposites, measured at a field of 7.05 T, using a recovery time of 3 to 5 s between scans.
Figure S8: Plot of the fraction of mobile ions of the nanocomposites at 30 °C as function of the mesopore diameter of their silica scaffolds. MCM-41-based nanocomposites are denoted by circles, SBA-15-based by crosses and those based upon fumed silica (which has no well-defined mesopores) by diamonds. The black line indicates the hypothetical fraction of mobile ions for perfectly cylindrical pores as function of the pore diameter $d$ via $4 (t d - t^2) / d^2$, assuming a mobile layer thickness $t$ of 0.5 nm (as found in our previous study for SBA-15-based nanocomposites$^{812}$). Clearly this hypothetical model does not cover the data points of nanocomposites based on MCM-41.

Figure S9: Diffuse reflectance infrared (DRIFTS) spectra of thin-walled (MCM-41-C$_{16}$-150-2) and thick-walled (MCM-41-C$_{16}$-180-2) silica after being dried at 300 °C. The peaks are assigned to isolated (about 3745 cm$^{-1}$) and vicinal (hydrogen-bonded, 3700-3000 cm$^{-1}$) silanol O–H vibrations, in accordance with literature.$^{813}$ There are no peaks in the C–H stretching region (3000-2900 cm$^{-1}$), indicating a proper removal of the organic template during calcination.
Figure S10: $^{29}$Si MAS NMR spectra of (a) the silica scaffold MCM-41-C_{16}-150-2 and (b) the nanocomposite MCM-41-C_{16}-150-2, as well as their deconvolutions into individual peaks. For assignment of the peaks, the reader is referred to figure 3 and the main text; the ratios of the peaks are listed in table 2. The experiments were performed on a field of 7.05 T at 3 and 6.5 kHz MAS respectively. The spectrum of the silica (a) is the sum of spectra with a fixed delay of 50000 and 86400 s between subsequent scans. The $^{29}$Si spin-relaxation time, which is longest for the $Q_4$ peak, is $T_{1Q_4}^* \approx 2 \cdot 10^4 \pm 1 \cdot 10^4$ s in this silica scaffold. The spectrum of the nanocomposite (b) was recorded with a fixed delay of 3600 s between scans; at longer delays between scans, (only) the $Q_4$ peak will gain more intensity (4 to 8 percent points), presumably due to silica that is at a large distance from LiBH$_4$.

Figure S11: {$^1$H}$^{29}$Si CP-MAS NMR spectra of silica of the type SBA-15, before and after being treated under melt-infiltration conditions (without LiBH$_4$). The spectra display excellent agreement, indicating no changes have occurred as a result of this treatment. The spectra were recorded on a field of 9.4 T at a spinning speed of 3.25 kHz. The weak spinning sidebands are indicated by asterisks.
Figure S12: $^1$H NMR spectrum of silica scaffold MCM-41-C$_{16}$-150-2 (without LiBH$_4$), measured using a Hahn echo at a field of 9.4T under 3.25kHz MAS. Spinning sidebands are indicated by asterisks. The peaks between 1.6 and 2.2 ppm are ascribed to silanol groups.$^{814}$
Table S4: Dipolar second moments and corresponding \((r^{-3}\)-weighted) average internuclear distances obtained from fits of \({}^7\text{Li}\)\(29\text{Si}\) and \({}^{11}\text{B}\)\(29\text{Si}\) REDOR curves of the nanocomposite MCM-41-C\(_{16}\)-150-2\(^{i}\) (figure S13). The REDOR curves were fitted to the analytical formula derived by Hirschinger to obtain the heteronuclear dipolar second moment and the average internuclear distance.\(^{515-517}\) As the quadrupolar interactions of \(^{11}\text{B}\) and \(^7\text{Li}\) in LiBH\(_4\)/SiO\(_2\) nanocomposites are small, the REDOR experiment can be used quantitatively.\(^{518}\) The margin in the least-squares fit of the second moment is typically 20-30\%, resulting in an error of approximately 0.3 Å in the distance. This excludes the error in the REDOR curve, and assumes each lithium or boron atom couples with only one silicon atom of a certain species. The data of \(Q'_3\) may include a contribution of isolated SiOH or SiH sites, but this contribution is expected to be small.

| Nuclei       | Second moment (kHz\(^2\)) | Internuclear distance (Å) |   |
|--------------|---------------------------|---------------------------|---|
| mii \(\text{Si}{}^7\text{Li}\) | 2.1 2.3 0.25 | 3.4 3.4 4.9 |   |
| mii \(\text{Si}{}^{11}\text{B}\) | 1.1 0.23 0.21 | 3.6 4.6 4.7 |   |

Figure S13: Least-squares fits of the (a) \({}^{11}\text{B}\)\(29\text{Si}\) and (b) \({}^7\text{Li}\)\(29\text{Si}\) REDOR difference curves of LiBH\(_4\)/SiO\(_2\) nanocomposites, shown in figure 5. The curves were fitted to the formula derived by Hirschinger\(^{515}\), and assume a single, homogeneous dipolar interaction with either \({}^{11}\text{B}\) or \(^7\text{Li}\) per silicon site. Although the error bars are significant, visual inspection suggests the fits underestimate the curve at longer recoupling times for mii and \(Q'_3\) sites, which is likely the result of inhomogeneity in the dipolar couplings.
Figure S14: Figure showing the effect of the physisorption pore size distribution model (DFT or BJH) and the influence of the XRD reflection (either (100) or (200)) used to calculate the pore wall thickness. The black circles are equal to the data shown in figure 6.

Figure S15: $^{1}H^{29}Si$ LGCP build-up curves of (a) thin (MCM-41-C$_{16}$-150-2$^{i}$) and (b) thick (MCM-41-C$_{16}$-180$^{i}$) walled MCM-41-based nanocomposites, normalized to the maximal peak integral, or 4 ms if the maximum was not reached yet. The spectra were measured at a field of 9.4 T under 6.5 kHz MAS.
Figure S16: Normalized $^{11}$B MAS NMR spectra of thin (MCM-41-C$_{16}$-150-2) and thick (MCM-41-C$_{16}$-180-2) walled MCM-41-based nanocomposites. The experiment was performed at 12.5 kHz MAS in a field of 9.4 T. Insets contain the spectrum in the region of the BH$_{4}^{-}$ peaks. Spinning sidebands of LiBH$_{4}$ are indicated by asterisks. The small peaks between 20 and $-35$ ppm correspond mostly to oxidations of LiBH$_{4}$ as demonstrated in the supporting information of our previous study.$^{S12}$ The highly dynamic and more bulk-like LiBH$_{4}$ fractions resonate at $-40.5$ and $-41.3$ ppm, respectively.$^{S19}$ The chemical shift of the bulk-like fraction is equal to the chemical shift of bulk LiBH$_{4}$.$^{S20}$

![Normalized $^{11}$B MAS NMR spectra](image)

Figure S17: Change in volume of the silica upon applying pressure. The volume change was measured in-situ in a 13 mm pellet die. The silicas shown are MCM-41-C$_{16}$-150-2 (thin-walled MCM-41), MCM-41-C$_{16}$-180-2 (thick-walled MCM-41) and SBA-15-120. For comparison: the volume change of Aerosil 380 (not shown) was about $-8$ mL/g at a pressure of 38 MPa, then stabilizing at $-8.5$ mL/g at higher pressures.

![Change in volume of the silica](image)
Semi-quantitative approach to determine whether the mii-peak is proportional to the interface between LiBH₄ and silica or to the total composition of the nanocomposite.

Although CP-MAS experiments are not inherently quantitative, it is possible to do a rough quantitative comparison of the mii-peaks in the nanocomposites MCM-41-C₁₆-150-2 (thin pore walls) and MCM-41-C₁₆-180-2 (thick pore walls), as the cross-polarization dynamics are comparable for both nanocomposites (figure S15).

After normalization to equal number of molecules per NMR rotor (using the ⁷Li integrals and the sample composition) and the number of scans, the ratio between the mii-peaks of the nanocomposites with thin and thick silica pore walls was:

\[
\frac{I_{mii}^{\text{thin}}}{I_{mii}^{\text{thick}}} \approx 0.5
\]

We now consider two hypothetical cases:

1. **The mii-peak is proportional to the surface area of the silica.** In this case, the peak would be expected to scale with the surface area \((BET, \text{m}^2/\text{mole})\) of the silica scaffold, and the molar ratio between silica and LiBH₄ \(f_{SiO_2} = n_{SiO_2}/(n_{LiBH_4} + n_{SiO_2}) \propto n_{SiO_2}\), the latter step due to normalization), i.e., doubling of the surface area per amount of silica or doubling the amount of silica (which would both double the total surface area) would result in a doubling of the mii peak. This assumes sufficient LiBH₄ is present to wet the entire silica surface. This hypothetical case would yield a ratio of:

\[
\frac{I_{mii}^{\text{thin}}}{I_{mii}^{\text{thick}}} \propto \frac{BET_{thin}}{BET_{thick}} \cdot \frac{f_{SiO_2}^{\text{thin}}}{f_{SiO_2}^{\text{thick}}} \approx 1.9
\]

2. **The mii-peak is proportional to the total amount of silica.** In this case, the peak would roughly scale with the fraction of silica in the nanocomposite. This case would yield a hypothetical ratio of:

\[
\frac{I_{mii}^{\text{thin}}}{I_{mii}^{\text{thick}}} \propto \frac{f_{SiO_2}^{\text{thin}}}{f_{SiO_2}^{\text{thick}}} \approx 0.7
\]

Clearly, the hypothetical ratio for an interaction involving the total amount of silica is much closer to the experimentally determined ratio, than an interaction involving only the interface between lithium borohydride and silica. It should be noted that these are rough approximations: i.e. pore filling deficiencies are not taken into account.
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