The role of Ni in increasing the reversibility of the hydrogen release from nanoconfined LiBH₄

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Supplementary information

Porosity of the carbon in the nanocomposites (Nitrogen physisorption)

Figure S1. Nitrogen adsorption isotherms (A) and pore size distribution (B) of pure HSAG-500 carbon, 5wt% Ni/C, and nanocomposites 25LiBH₄/C and 25LiBH₄/3.75NiC.

Fig. 1(A) shows that after melt infiltration with 25 wt% LiBH₄, the accessible pore volume has decreased drastically. Figure 1(B) illustrates that most of the micropores and also the mesopores were filled upon melt infiltration. The total pore volume decreased from 0.66 cm³/g [C] to 0.11 cm³/g [C]. This corresponds to 84% pore filling, in line with the volume of LiBH₄ in the nanocomposites. No noticeable difference exists between the sample containing Ni and the sample without Ni.
TEM measurements

Figure. S2 TEM image of (A) 5wt% Ni/C and (B) 25LiBH₄/3.75Ni/C nanocomposites after synthesis The electron diffraction pattern shown on the right was taken on the area of the sample shown on the left.

The diffraction rings are analysed using

\[ \lambda L = Rd \]  

Where \( \lambda L \) is the camera constant of the TEM = 720, \( R \) is the ring diameter and \( d \) is the d-spacing of the substance measured. Since \( \lambda L \) is a constant, this implies that

\[ R_1d_1 = R_2d_2 = R_3d_3 = R_nd_n \]  

For graphite \( d_1 = 3.34\text{Å}, d_2 = 1.68 \text{Å} \) and \( d_3 = 1.54 \text{Å} \)

For Ni, \( d_1 = 2.03 \text{Å}, d_2 = 1.76 \text{Å} \) and \( d_3 = 1.25 \text{Å} \).

From Figure 2(A), there are scattered diffraction rings however the ring diameters that can be identified are
R₁ = 307 mm, R₂ = 422.57 mm, R₃ = 498.89 mm, R₄ = 532.83 mm and R₅ = 582.15 mm

For Ni, it can be shown that

\[ R_1 d_1 = (307 \times 2.03) \approx R_3 d_3 = (1.25 \times 498.89) = 623, \]

which corresponds to the Ni d spacing of 2.03 and 1.25 Å

Also for the graphite, it can be shown that

\[ R_4 d_2 = (532.83 \times 1.68) \approx R_5 d_3 = (1.54 \times 582.15) = 895. \]

Therefore, for the 5wt% Ni/C, two diffraction rings due to Ni (d values of 2.03 and 1.25 Å) can be seen and two diffractions from the graphite (d values of 1.68 and 1.54 Å) can be resolved.

From Figure 2(B), the diffraction rings have diameter \( R_1 = 417.71 \) mm and \( R_2 = 449 \) mm

Substituting these values into equation 2

\[ 417.71 \times 1.68 \approx 449 \times 1.54 \]

Therefore the diffraction ring is due to the graphite d spacing of 1.68 and 1.54 Å showing that the Ni is amorphous after synthesis.

**EDX**

![EDX signal from LiBH₄/Ni/C nanocomposites (sample 2B) showing the presence of Ni.](image_url)
Figure S4. Magnitude and Imaginary part of the phase-uncorrected Fourier transformed $\chi(k)$ for the as-synthesized LiBH$_4$/Ni/C nanocomposites. The fit is optimized with $\Delta k=3-13$ Å$^{-1}$ and $\Delta R=1.2-3.0$ with the k-weighting parameter of 2. The individual contributions of Ni-B and Ni-Ni are also included.