

Supporting Information

Li-decorated BC₃ nanopores. Promising materials for hydrogen storage

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1. Local minima of the interaction potential and comparison of the potentials obtained with the different exchange-correlation functionals

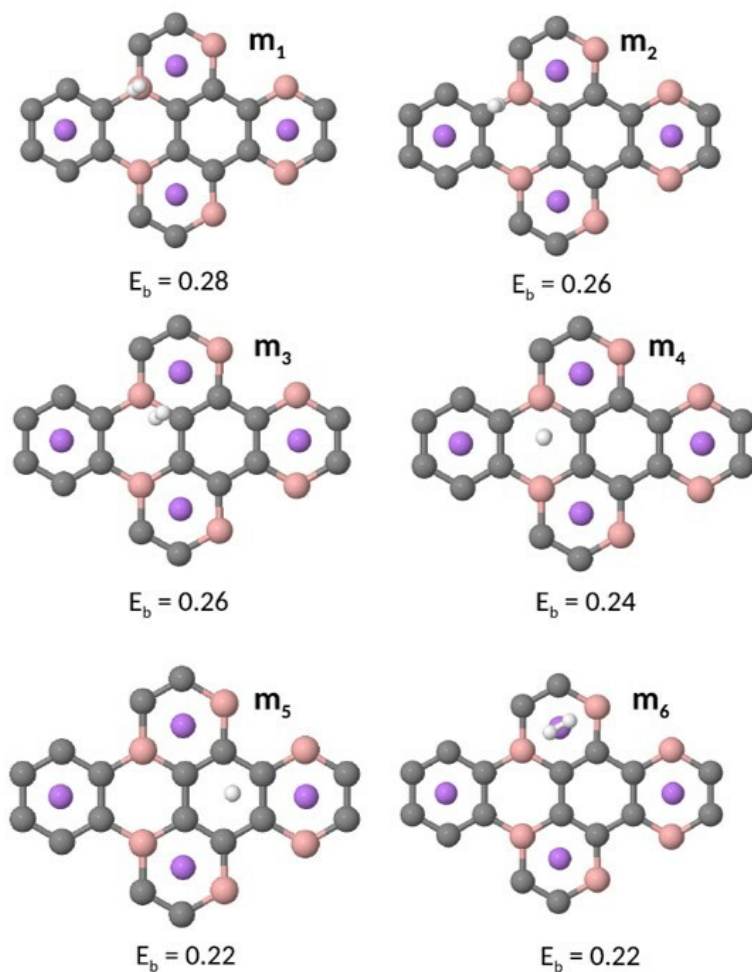


Fig. S1: System composed by the Li-decorated BC_3 sheet and the H_2 molecule at the six main local minima of the interaction potential. We show the values of H_2 -binding energies (i.e., the sign-reversed potential energies) in eV.

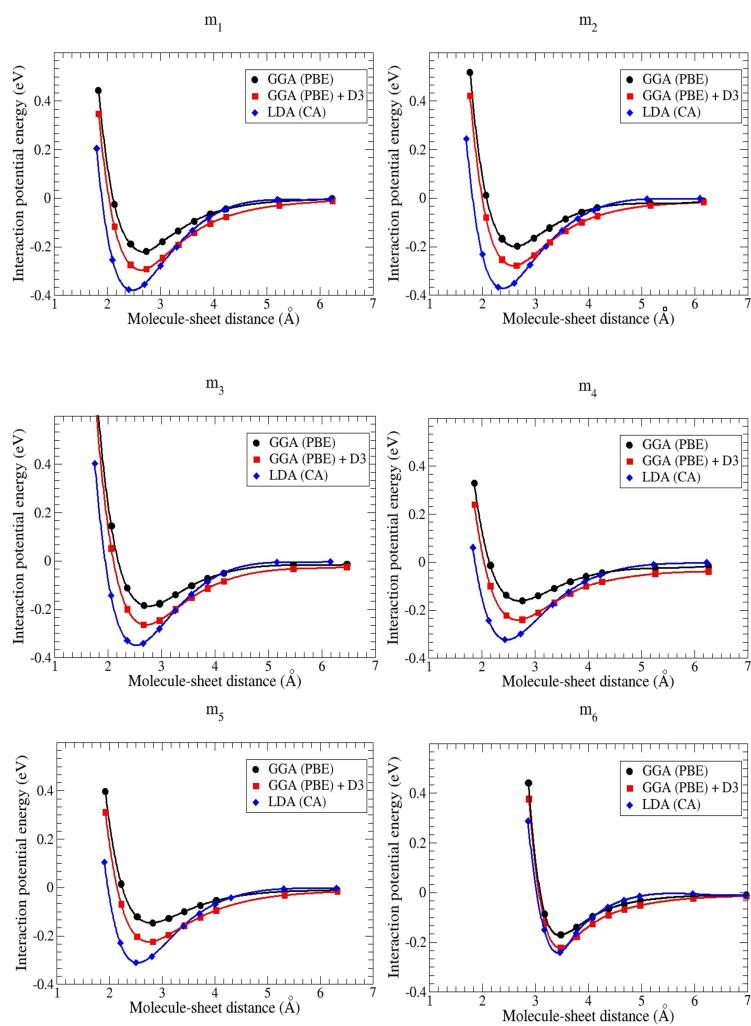


Fig. S2: Interaction potential curves around the six main local minima, as obtained with the three different exchange-correlation functionals.

2. Exact and approximated relationships between the adsorbed volumetric and gravimetric hydrogen storage capacities

There is an exact relationship between the adsorbed volumetric and gravimetric hydrogen storage capacities. According to Eq. 6 of the main text, the mass of the adsorbed hydrogen is given by $mass_{H\ adsorbed}(P, T) = v_c(P, T) V_{\text{pore}}$. In the case of slit-shaped pores, $mass_{\text{adsorbent material}} = \sigma_{\text{ads}} 2S$, where σ_{ads} is the mass surface density of a sheet of the slit pore and S is the surface of one sheet. The origin of the factor 2 is that the slit pore is formed by two sheets. Hence, Eq. 8 of the main text can be written exactly as

$$g_c = \frac{100v_c w}{v_c w + 2\sigma_{\text{ads}}} = \frac{100x}{x + 1}, \quad (\text{S1})$$

being $x = v_c w / 2\sigma_{\text{ads}} > 0$, a dimensionless magnitude.

We now note that the adsorbed volumetric capacity as a function of the pore width w has some maximum and then decreases slowly towards a constant value (see Fig. 7 of the main text). Hence, according to the exact Eq. S1, the adsorbed gravimetric capacity is an increasing function of the variable x , but not an increasing function of w . To be more precise, g_c is an increasing function of the product $v_c w$, since the mass surface density, σ_{ads} , is constant for slit pores of the same type, as can be noticed in Table S1.

Table S1: The mass surface densities, σ_{ads} , of some sheets in 10^{-26} kg/Å².

Sheet	σ_{ads}
Graphene	0.76
Li-decorated BC ₃	0.73

The ranges of values of the adsorbed volumetric capacity, the pore width and the product of these two quantities are shown in Table S2.

Table S2: Ranges of values of the adsorbed volumetric capacity v_c at 77-298.15 K and 0.1-25 MPa, in kg/L, of the pore width w , in Å, of the product $v_c w$, in 10^{-26} kg/Å², and of the dimensionless magnitude $x = v_c w / 2\sigma_{\text{ads}}$, for different types of slit pores.

v_c	w	$v_c w$	x
0.001-0.08	5-100	0.0005-0.8	0.0002-0.4

The data in Tables S1 and S2 prove that $v_c w$ is smaller or much smaller than $2\sigma_{\text{ads}}$. The dimensionless magnitude x in Table S2 shows how much small is $v_c w$ compared to $2\sigma_{\text{ads}}$: it is between 0.0002 and 0.4. Therefore, it is a reasonable approximation to make $x/(x + 1) \approx x$ for graphene and Li-decorated BC₃ slit pores with a small value of x . Applying this approach to Eq. S1, we obtain the approximate equation

$$g_c \approx 100x = 100 \frac{v_c w}{2\sigma_{\text{ads}}}. \quad (\text{S2})$$

The exact and the approximated (Eq. S2) adsorbed gravimetric capacities for Li-decorated BC₃ slit pores at 298.15 and 25 MPa are compared in Fig. S3. As it can be noticed, the approximation is very good.

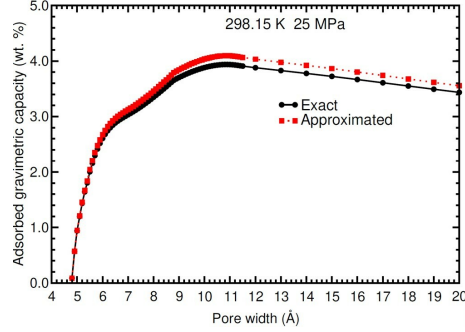


Fig. S3: Exact and approximated (Eq. S2) adsorbed gravimetric capacities of Li-decorated BC_3 slit pores as functions of the pore width at 298.15 K and 25 MPa.

When comparing the adsorbed gravimetric capacities of graphene and Li-decorated BC_3 slit pores, it must be taken into account that the surface densities of their corresponding sheets are very similar (see Table S1). Hence, the differences in the adsorbed gravimetric capacities of the slit pores can be mainly ascribed to differences in the adsorbed volumetric capacities. Inserting the approximation $\sigma_{\text{graphene}} \approx \sigma_{\text{Li-decorated}BC_3}$ into Eq. S2, it can be obtained, for the same pore width w , the approximated equation

$$\frac{g_c(BC_3Li)}{g_c(\text{graphene})} \approx \frac{v_c(BC_3Li)}{v_c(\text{graphene})}. \quad (\text{S3})$$

In order to test this equation, we have plotted in Fig. S4 the ratio of the adsorbed gravimetric capacities, $\frac{g_c(BC_3Li)}{g_c(\text{graphene})}$, vs the ratio of adsorbed volumetric capacities, $\frac{v_c(BC_3Li)}{v_c(\text{graphene})}$, at 298.15 K and 25 MPa for pore widths between 4.6 and 20 Å. The graph proves that Eq. S3 is very well satisfied. That equation contains two approximations explained before: $x/(x+1) \approx x$, where $x = v_c w / 2\sigma_{ads}$, and $\sigma_{\text{graphene}} \approx \sigma_{\text{Li-decorated}BC_3}$.

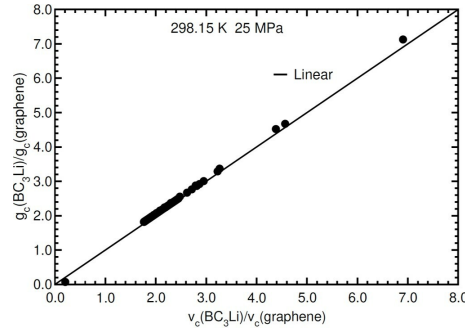


Fig. S4: Comparison of the ratio of the adsorbed gravimetric capacities with the ratio of the adsorbed volumetric capacities of graphene and Li-decorated BC_3 slit pores at 298.15 K and 25 MPa for pore widths between 4 and 20 Å.

3. Location of highest gravimetric capacity

According to Eq. S2, the adsorbed gravimetric capacity is approximately proportional to the product $v_c w$. Therefore, the maximum value of g_c is not located at the maximum value of v_c , but at the maximum value

of $v_c w$. Let's call w_{maxg_c} the value of the pore width for which the maximum of g_c is found. The derivative of g_c with respect to w must be zero at that point. This implies that

$$\left. \frac{dv_c}{dw} \right|_{w=w_{maxg_c}} w_{maxg_c} + v_c(w_{maxg_c}) = 0 . \quad (S4)$$

This equation turns into

$$w_{maxg_c} = - \frac{v_c(w_{maxg_c})}{\left. \frac{dv_c}{dw} \right|_{w=w_{maxg_c}}} . \quad (S5)$$

Now, we focus in the region in which $w > w_{maxv_c}$, where w_{maxv_c} is the location of the maximum of the volumetric capacity. The derivative of v_c with respect to w is negative in that region (see Fig. 7 of the main text). Hence, Eq. S5 turns finally into

$$w_{maxg_c} = \frac{v_c(w_{maxg_c})}{\left| \left. \frac{dv_c}{dw} \right|_{w=w_{maxg_c}} \right|} . \quad (S6)$$

The absolute value of the derivative or slope of the adsorbed v_c in that region when the orientation of the H_2 molecule is not fixed is smaller than for the fixed orientation. Besides, in the mentioned region, v_c is larger for the non-fixed orientation than for the fixed orientation. Therefore, according to Eq. S6, the pore width corresponding to the maximum of the adsorbed gravimetric capacity (w_{maxg_c}) for the non-fixed orientation is larger than for the fixed orientation, i.e., the highest adsorbed gravimetric capacities for the non-fixed orientation are located at larger pore widths, as it can be observed in the results shown in Fig. 7 and Table 1 of the main text.

4. Additional results for the total and usable hydrogen storage capacities of Li-decorated BC₃ slit pores

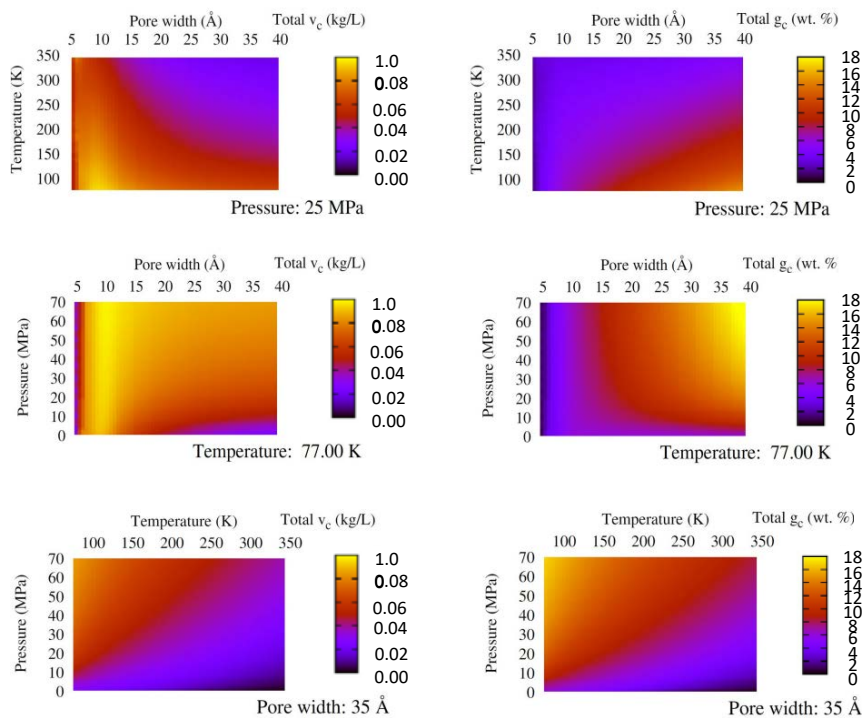


Fig. S5: Total volumetric and gravimetric hydrogen storage capacities of Li-decorated BC₃ slit pores as functions of the pore width and temperature at 25 MPa (upper panels), of the pore width and pressure at 77 K (middle panels), and of the temperature and pressure for a pore width of 35 Å (lower panels).

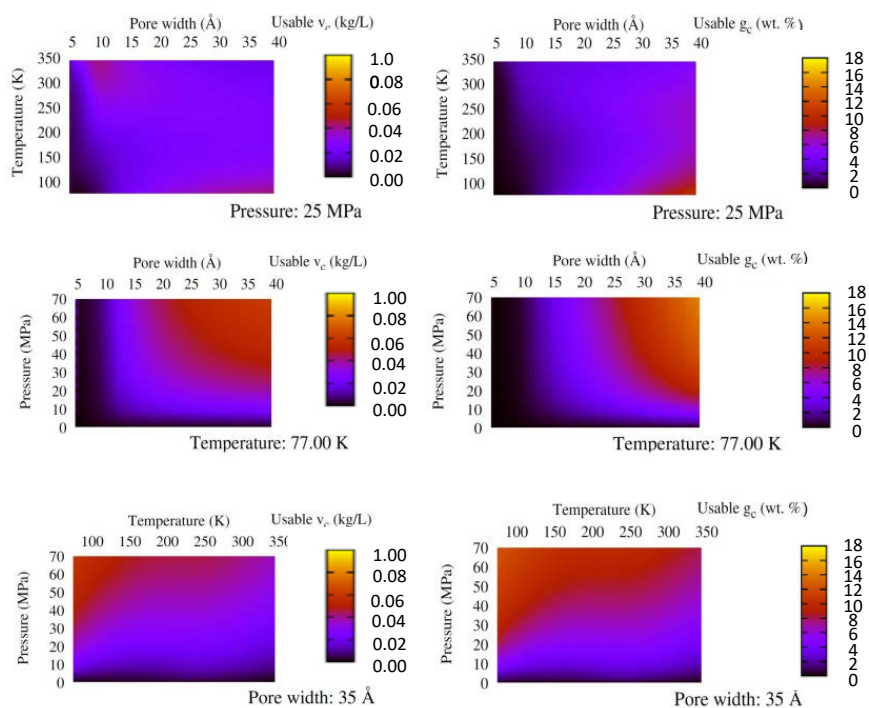


Fig. S6: Usable volumetric and gravimetric hydrogen storage capacities of Li-decorated BC_3 slit pores as functions of the pore width and temperature for 25 MPa (upper panels), of the pore width and pressure for 77 K (middle panels) and of the temperature and pressure for a pore width of 35 Å (lower panels).

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