Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Monolayer BC_2: an ultrahigh capacity anode material for Li ion batteries

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Phonon spectra and formation energies of BC_x sheets

Among uniformly doped BC_x sheets, BC_3[1] and BC5[2] have been experimentally synthesized. The structure of BC7 has also been theoretically predicted and shown to be stable.[3] We have calculated the phonon spectra for BC_2 sheet as shown in Fig. S1 (a). The absence of negative frequency confirms the dynamic stability of the sheet. Three non-uniformly doped BC_x sheets (BC_5-II, BC_2-II and BC-II), studied here, are reported to be dynamically stable according to their phonon spectrum.[4]

Furthermore, thermodynamic stability of uniformly doped BC_x sheets has been investigated by calculating the formation energy ($E_f(BC_x)$) using the following formula:

$$E_f(BC_x) = E_{BC_x} - x\mu_C - \mu_B \quad (1)$$

where E_{BC_x} is the total energy for BC_x sheet, μ_C and μ_B are chemical potentials of C and B referenced to the total energies of graphene and α-boron structure,[5] respectively. As shown in Fig. S1 (b), although the formation energies are positive, the values are very small indicating the possibility of synthesizing these sheets on a substrate. The formation energy is the lowest for BC_3 followed by BC_7 and BC_5. BC_2 has higher formation energy compared to these three sheet while BC shows the highest value. Given the fact that BC_3 and BC_5 are already being synthesized, there is a great chance that BC_2 can also be synthesized.

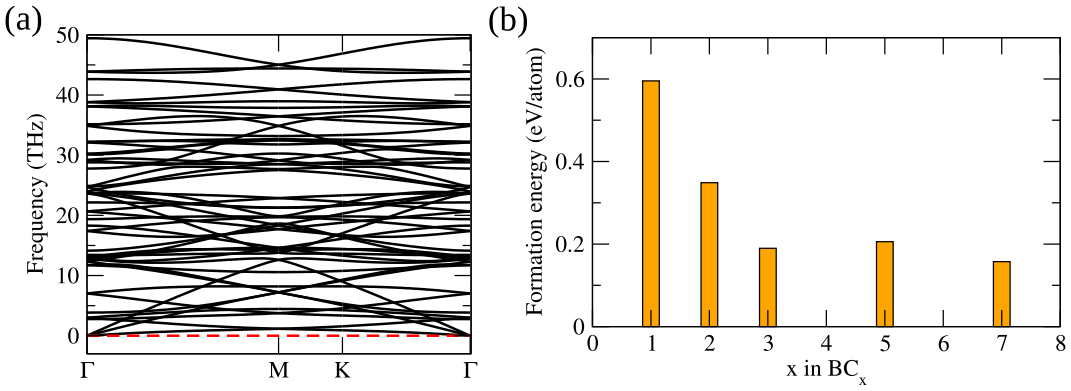

Fig. S1: (a) Phonon spectra for uniformly doped BC_2 sheet and (b) plot of formation energies per atom for different uniformly doped BC_x sheets.

Structures after one Li adsorption:

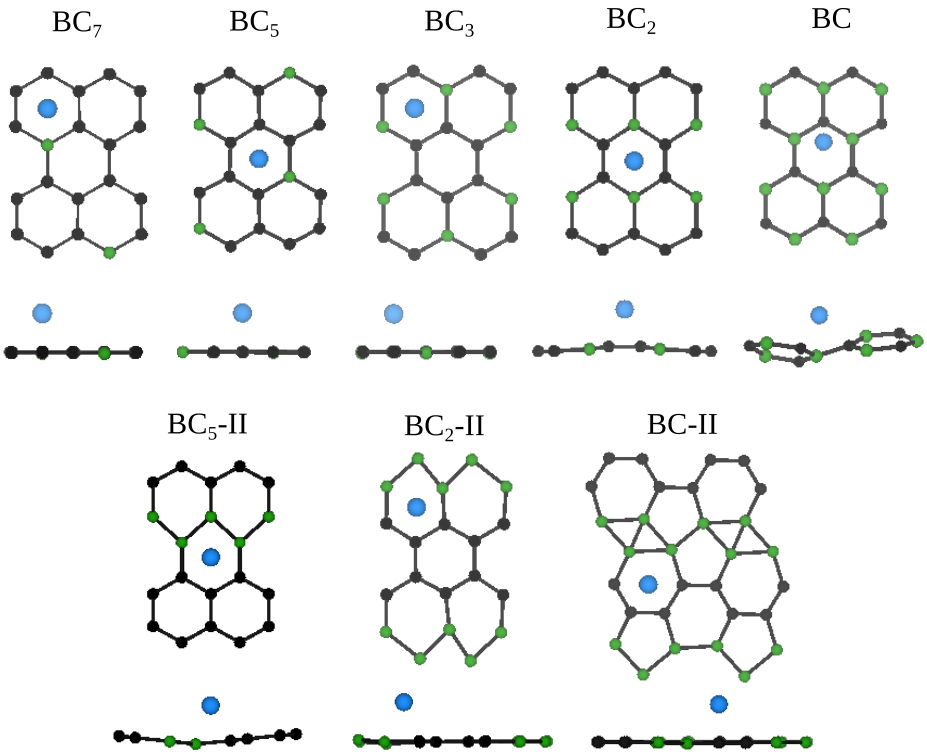

Fig. S2: Uniformly doped (upper panel) and non-uniformly doped (lower panel) BC_x structures after adsorbing one Li

Potential energy surface for Li diffusion:

A scan of the potential energy surface for Li across the plane of BC_x sheets is carried out. In Fig. S3, these potential energy surfaces are plotted for (a) BC_2, (b) BC_5, (c) BC_7, (d) BC_5-II, (e) BC_2-II and (f) BC-II sheets. The dark valleys indicate the lowest energy barrier while the bright areas indicate a finite energy barrier. The regions having same energy barriers are marked with contours in Fig. S3. Li diffuses along the path connecting energy minima with low energy barriers. The energy barrier gradually increases as B concentration reduces in the uniformly doped sheets.

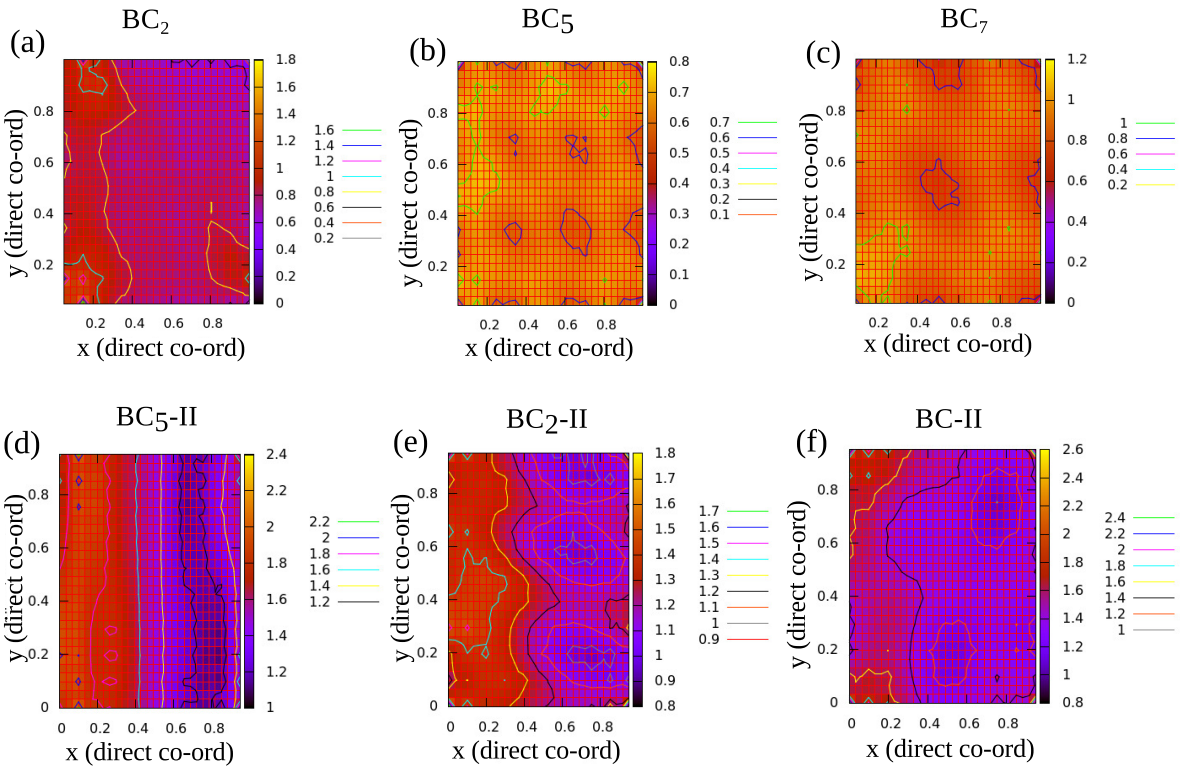

Fig. S3: Potential energy surface for the Li to diffuse over (a) BC_2, (b) BC_5, (c) BC_7, (d) BC_5-II, (e) BC_2-II and (f) BC-II, respectively. The dark valleys indicate the lowest energy barrier while the bright areas indicate a finite energy barrier.

Lithium saturated phases of BC_x sheets:

During lithiation, the point at which the slope of incremental formation energy changes from negative to positive, indicates the Li saturation denoting the sheet can not absorb more Li. The Li-saturated phases for BC_2, BC_5, BC_5-II and BC_7 sheets are shown in Fig. S4 below. The upper and lower panel denote one and two-sided lithiation, respectively. In uniformly doped BC_2, multilayer Li adsorption happens which leads to its remarkably high specific capacity.

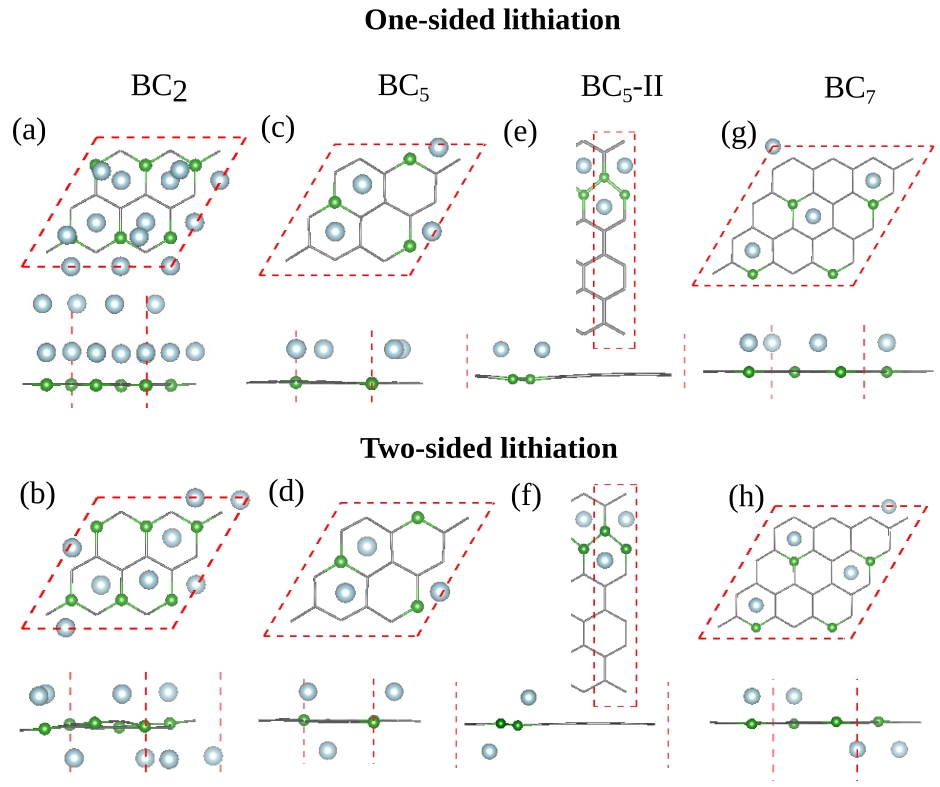

Fig. S4: Lithium saturated phases for one-sided lithiation and two-sided lithiation: (a-b) BC_2, (c-d) BC_5, (e-f) BC_5-II and (g-h) BC_7. Both top and side views have been shown for each case. Doped boron and Li atoms are shown by green and blue spheres, respectively.

Thermal stability using AIMD simulations:

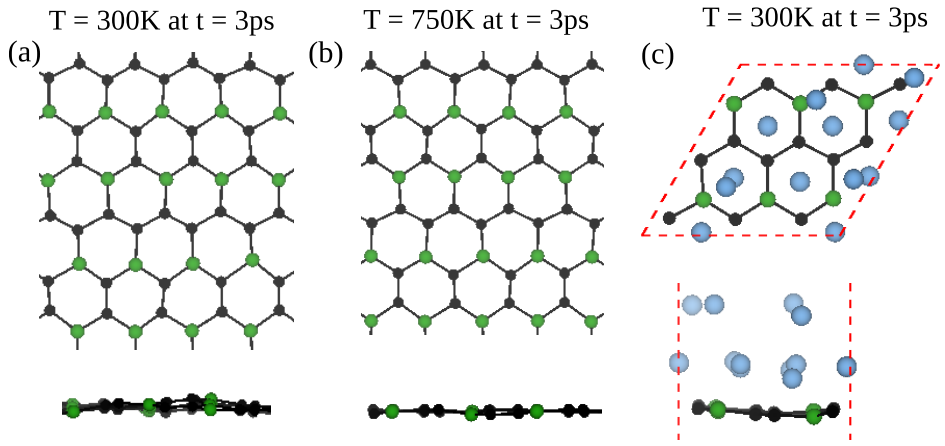

Fig. S5: Structures of BC_2 sheet at 300 and 750 K and its Li saturated phase at 300 K obtained using AIMD simulations to assess thermal stability

Partial density of states (PDOS) of B-2p and Li-2s states:

During lithiation, the B-2p and Li-2s states in uniformly doped BC_3, BC_5 and BC_7 sheets are plotted in Fig. S6. The trend is similar to uniformly doped BC_2 as discussed in the main paper. With increasing number of Li, the available B-2p states above the Fermi level decreases and becomes almost zero at the saturation (the sheet stops to adsorb Li anymore). This trend of shifting the states towards left (indicating the filling of the empty states by electron of Li) remains same. The Li-2s peak in the conduction band shifts left and crosses the Fermi level as number of adsorbed Li increases.

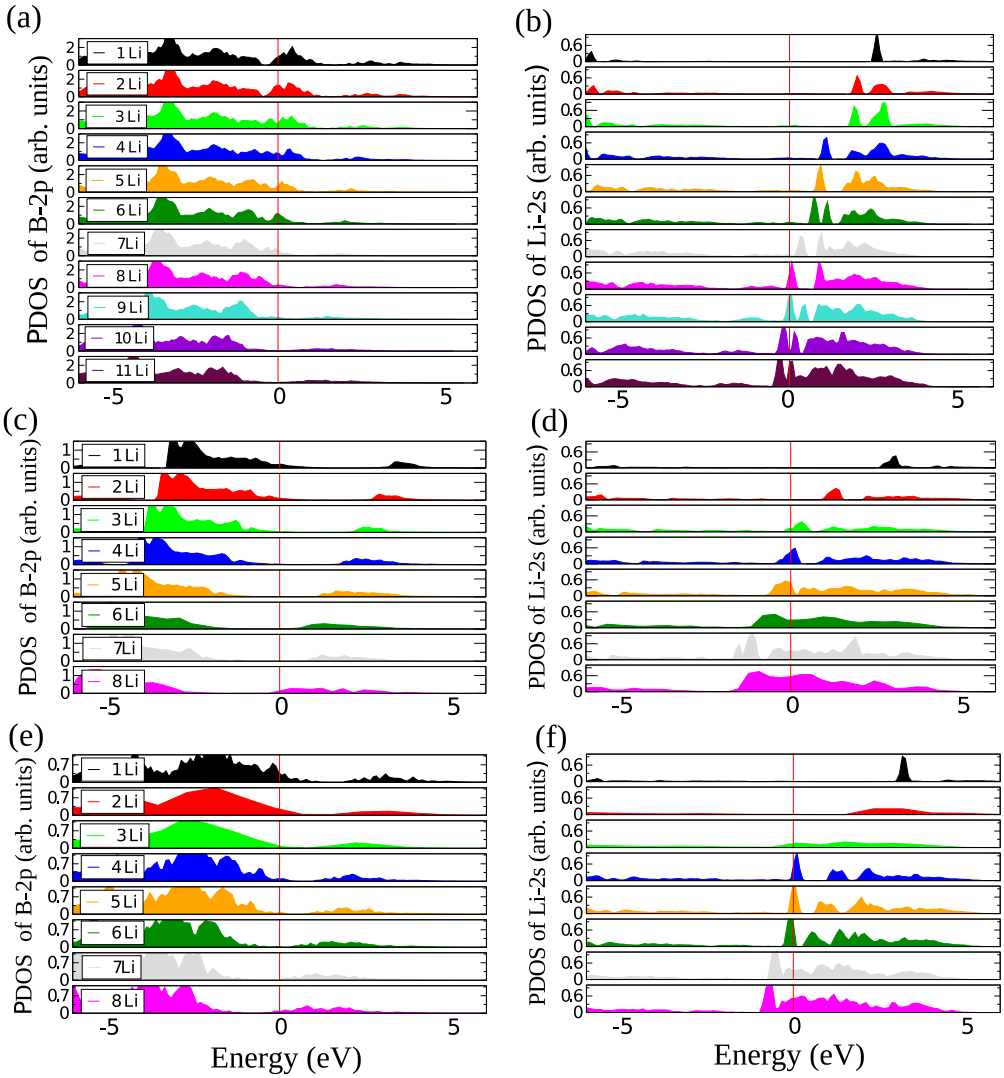

Fig. S6: Change in partial density of states for B-2p and Li-2s in uniformly doped (a-b) BC_3, (c-d) BC_5 and (e-f) BC_7 as a function of Li concentration during lithiation.

References

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