

Thermodynamic Insights into Polymorphism-Driven Lithium-Ion Storage in Monoelemental 2D Materials

Arnab Kabiraj, Aninda J. Bhattacharyya, and Santanu Mahapatra*



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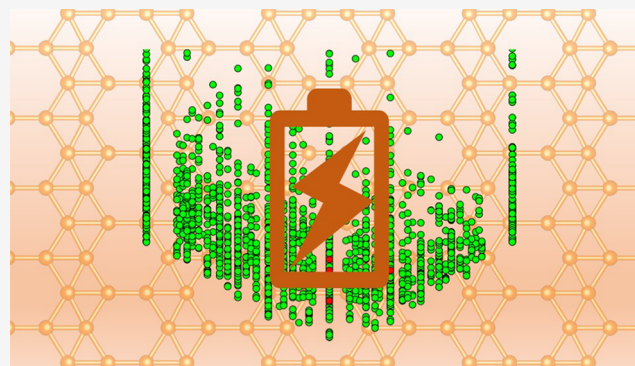


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Supporting Information

ABSTRACT: Monoelemental two-dimensional materials (borophene, silicene, etc.) are exciting candidates for electrodes in lithium-ion batteries because of their ultralight molar mass. However, these materials' lithium-ion binding mechanism can be complex as the inherited polymorphism may induce phase changes during the charge–discharge cycles. Here, we combine genetic-algorithm-based bottom-up and stochastic top-down structure searching techniques to conduct thermodynamic scrutiny of the lithiated compounds of 2D allotropes of four elements: B, Al, Si, and P. Our first-principles-based high-throughput computations unveil polymorphism-driven lithium-ion binding process and other nonidealities (e.g., bond cleavage, adsorbent phase change, and electroplating), which lacks mention in earlier works. While monolayer B (2479 mAh/g), Al (993 mAh/g), and Si (954 mAh/g) have been demonstrated here as excellent candidates for Li-ion storage, P falls short of the expectation. Our well-designed computational framework, which always searches for lithiated structures at global minima, provides convincing thermodynamical insights and realistic reversible specific-capacity values. This will expectedly open up future experimental efforts to design monoelemental two-dimensional material-based anodes with specific polymorphic structures.



Two-dimensional materials are being substantially explored for high-capacity Li-ion battery (LIB) anode materials because of their excellent surface-to-volume ratios.^{1,2} Specifically, light monoelemental 2D materials are promising candidates as they possess massive surface-to-mass ratios as well, leading to significant enhancement in the specific capacity of the electrode. Since the successful exfoliation of graphene from bulk graphite,³ many lightweight monoelemental 2D materials have been synthesized, such as borophene,^{4–6} silicene,^{7,8} and phosphorene.^{9,10} In parallel to experimental studies,¹ first-principles-based investigation using density functional theory (DFT) has been a tremendously popular choice to predict the essential figure of merits (FOM) of 2D materials as LIB anode.¹¹ These computational methods allow exploring a large set of materials, including those that have not been synthesized yet or have been synthesized under very stringent laboratory conditions, such as borophene. At the same time, such studies provide chemical insight into lithium binding at the atomic limit, which is difficult to probe even with a very sophisticated experimental setup. These predicted properties could act as strong guidelines for experimentalists. However, the calculated specific capacities are known to be drastically overestimated when compared to empirical findings.^{12,13} One reason for this could be using the “uniform adsorption” model in most of these studies. Recently, multiple high-throughput structure-searching-based computational

studies have demonstrated the “uniform adsorption” model's limits while predicting the most stable cation-adsorbed phase and the specific capacity.^{14,15} Another possible reason is that these studies cannot incorporate the nonideal effects of multiple charging–discharging cycles, such as bond breaking and formation, phase change of adsorbent, irreversible Li adsorption, electroplating, and so on. In such cases, the uniform-adsorption-predicted theoretical specific capacity might match experimental values for the first few cycles, but rapid capacity fading would soon reduce the quantity to a much lower reversible “effective capacity” which we have previously demonstrated for monolayer ReS₂.^{15,16}

Uniform-adsorption-based DFT studies have touted light monoelemental 2D materials as ultrahigh-capacity LIB anode materials. The important predicted values are 1250–5268 mAh/g for various polymorphs of borophene, up to 2680 mAh/g for 2D carbon allotropes, 954–1190 mAh/g for silicene, and up to 865 mAh/g for phosphorene allotropes, all

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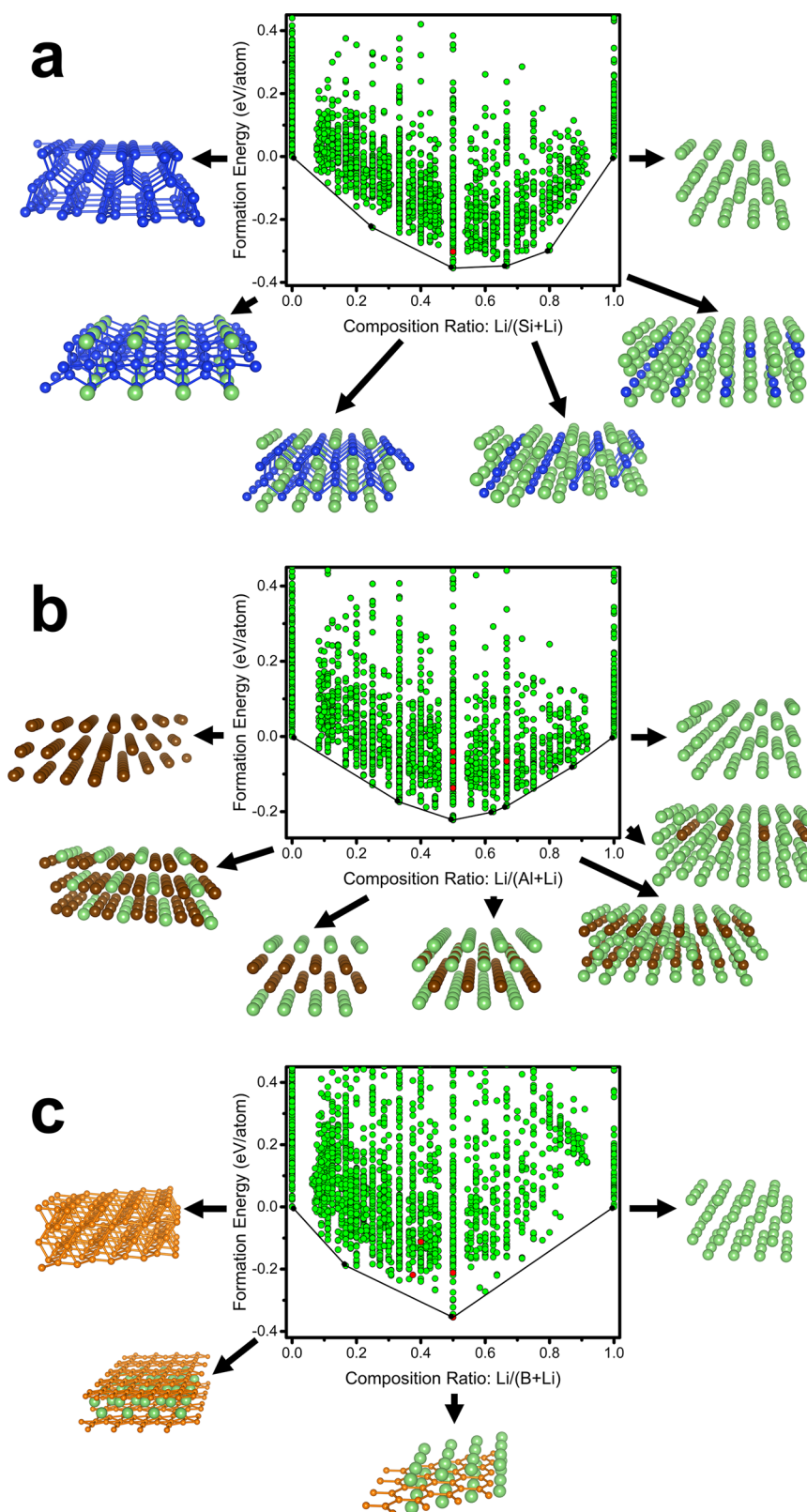


Figure 1. Bottom-up evolutionary structure-search-constructed convex hull for Li_xA_y composition space in the 2D limit along with most stable crystal structures. Here, (a), (b), and (c) depict Si, Al, and B, respectively. By convention, the lower the formation energy, the higher the stability. The red points in the plots signify the most stable lithiated structures found in this search for reported phases detailed in Figure 2. The blue, green, dark brown, and orange balls represent the Si, Li, Al, and B atoms.

of which are much higher than that of commercially used graphite anode.^{11,17} However, to the best of our knowledge, no experimental studies have been able to verify these ultrahigh

capacity predictions so far. Also, most of these materials exhibit a high amount of polymorphism, even at the 2D limit. The polymorphism of 2D carbon, boron, and phosphorus have

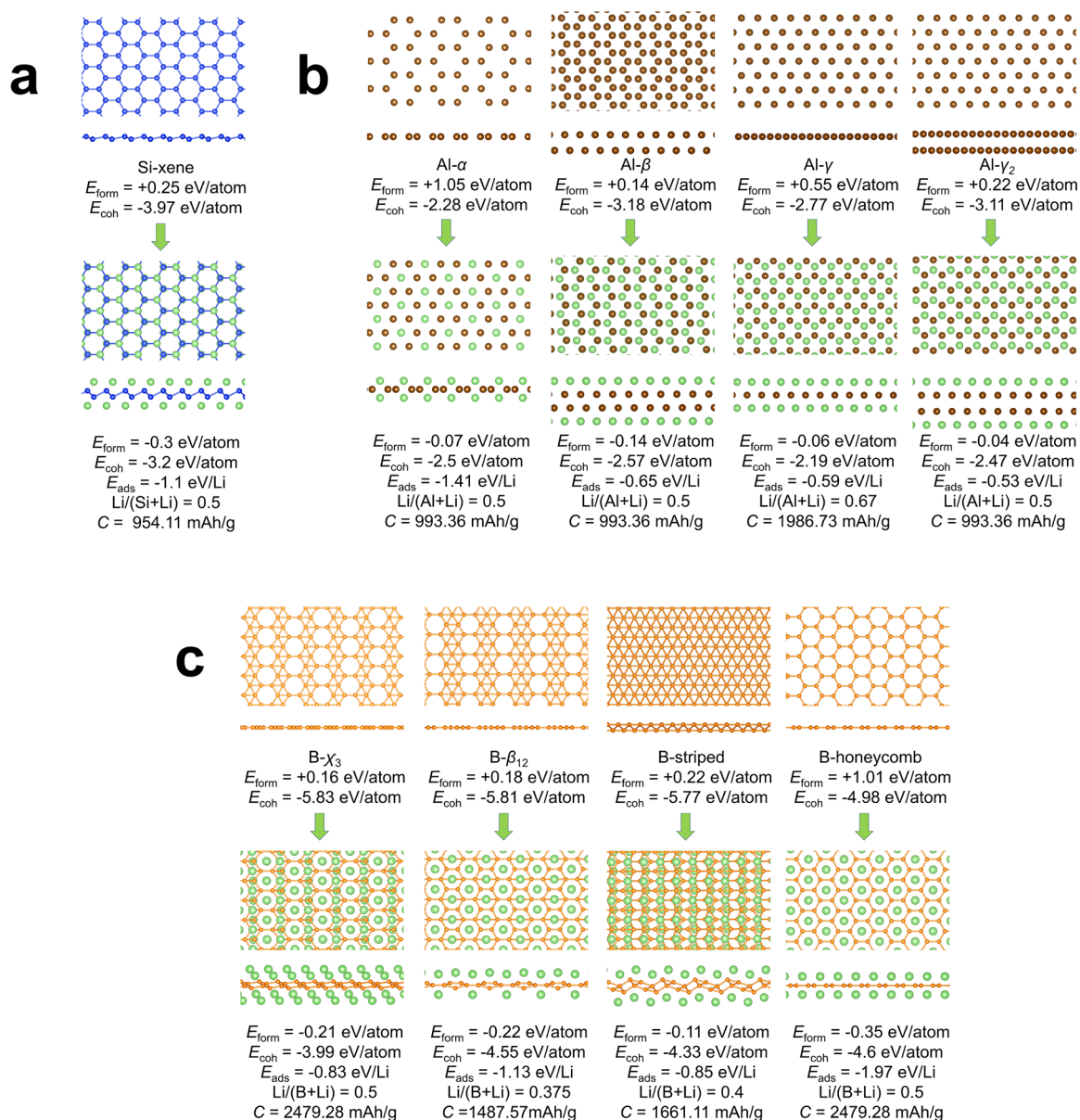


Figure 2. Reported 2D monoelemental allotropes and their most stable lithiated phases found in the bottom-up evolutionary structure-searching with relevant energetics and estimated storage capacities. Top and side view of reported 2D phases of Si, Al, and B with their lithiated structures, and relevant parameters are shown in (a), (b), and (c). The same color convention as Figure 1 has been used here.

been experimentally verified,¹¹ and a transition from one phase to another upon lithiation becomes a real possibility as the lithiation process can significantly alter the energy barriers. Such phase change (2H to 1T) with lithiation has already been reported for monolayer MoS₂,^{18,19} whereas in-situ and ex-situ microscopy studies have revealed semireversible bond cleavage and Li₂S and other compound formation in the case of MoS₂ and NbS₂ electrodes.^{19–21} Traditional computational studies lack the machinery to predict and explain such phenomena. Our recent top-down (starting with a known crystal structure of the host and adding Li ions to its surface) structure-searching-based study has been partially successful for ReS₂ and MoS₂ in this regard.¹⁵ Calculation of the formation energy of lithiated electrode compounds as a function of Li concentration and subsequent construction of the convex hull (i.e., thermodynamic assessment of the Li-electrode composition space) has become a popular tool to predict the

globally most stable lithiated phases and concurrently the figure of merits.^{12,14,22–26} Forcefully charging the electrode beyond the global energy minimum can induce irreversible changes that could ultimately result in significant capacity fading and even disintegration of the electrode material. This thermodynamic assessment process also takes care of the polymorphism while finding the global minimum, making it even more suitable to predict the figure of merits of monoelemental 2D materials-based LIB anode. However, the convex hull's construction must be done through a bottom-up (starting with random atomic configurations of Li and the element under study) search to explore all possible, stable lithiated phases. This kind of convex hull can be used as a “map” by experimentalists that allow drawing a fair comparison of the thermodynamic stability of different lithiated mono-elemental 2D phases, in terms of both Li concentration and polymorphism, making it easier to synthesize and test these

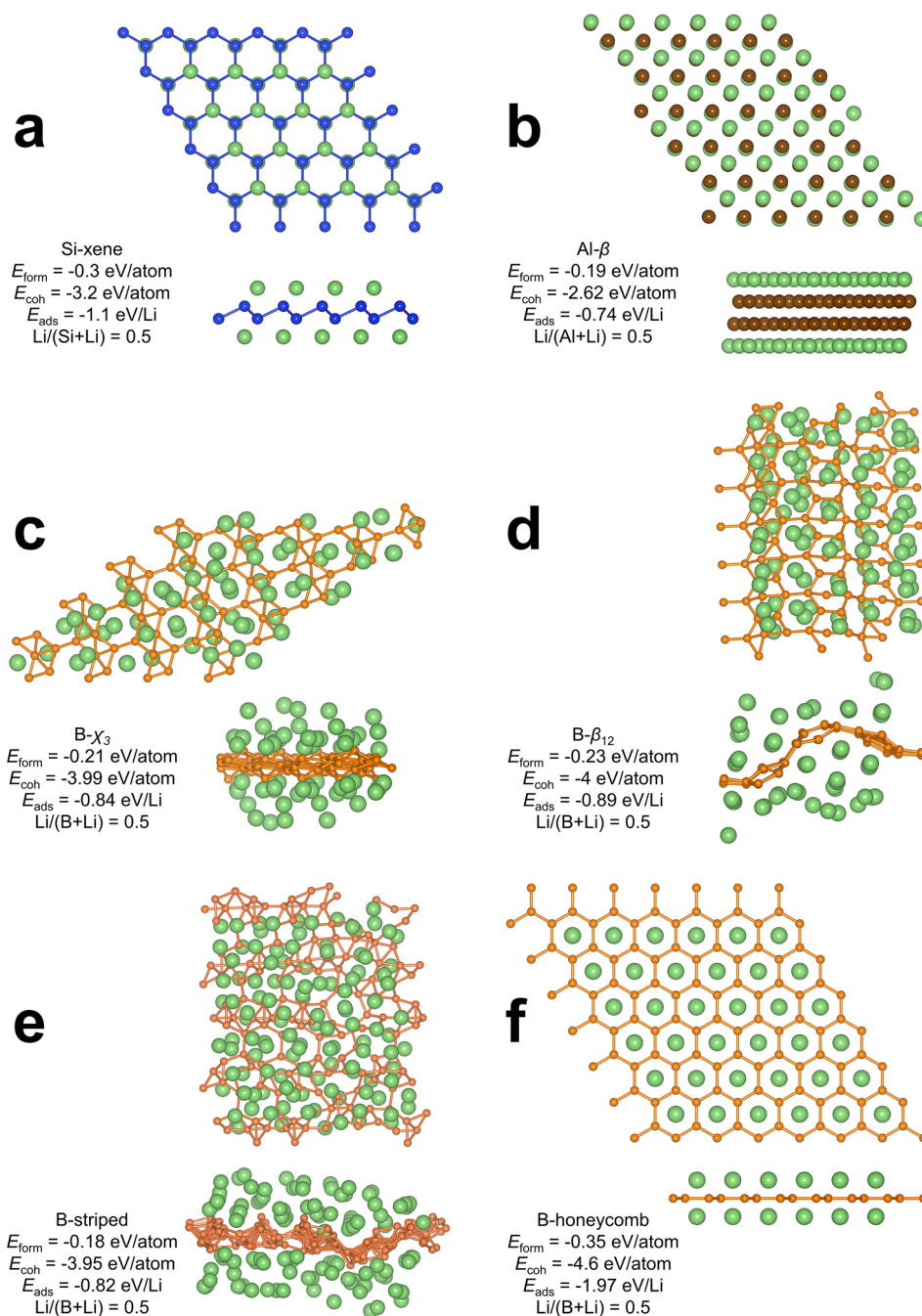


Figure 3. Top and side view of most stable lithiated phases of promising allotropes found by top-down AIRSS with relevant energy and concentration parameters. Lithiated lowest-energy Si-xene, Al- β , B- χ_3 , B- β_{12} , B-stripped, and B-honeycomb phases are shown in parts (a), (b), (c), (d), (e), and (f), respectively.

systems. On the other hand, top-down structure-searching-based studies begin with an individual phase and predict the most stable lithiated structure at a particular Li concentration, which often turns out to be not a uniformly adsorbed but a severely deformed system.^{14,15,27} Once an estimate of the global minimum is obtained through a bottom-up search with a small number of atoms, the precise local minima can be determined with a many-atom top-down structure search.

We have chosen four of the lightest elements in this work, viz., B, Al, Si, and P (and C for completeness), whose 2D structural forms have been explored by using experiments and predicted computationally.^{11,28,29} A bottom-up evolutionary structure-searching algorithm³⁰ is used to test their lithiated

compounds' relative thermodynamic stability in the 2D limit. In addition, stability tests for promising B, Al, and Si phases are performed by using large-supercell top-down ab initio random structure searching (AIRSS)³¹ algorithm and ab initio molecular dynamics (AIMD) studies. From these exercises, a realistic estimate of the reversible specific capacity for the mono-elemental 2D materials is determined that for some cases turned out to be much less than the previous theoretical predictions. Several counterintuitive results are also revealed. For instance, the uniformly adsorbed lithiated silicene became the most stable phase by both top-down and bottom-up approaches. We also observe the lithiation inducing phase change in aluminene and borophene. Moreover, lithiated

graphene-like honeycomb borophene turned out to be the most stable phase in the whole Li_xB_y composition space, despite the pristine honeycomb phase being the most unstable borophene by quite a distance.

We use an evolutionary structure searching³⁰ algorithm to find the global energy minimum of the Li_xA_y composition space ($\text{A} = \text{B/C/Al/Si/P}$) in the 2D limit, i.e., the whole system being only a few atomic layers thin. As several thousand (>5000 for each space) structures need to be searched and probed for the precise assertion of the global minimum structure, the total number of atoms per structure is kept in the range $2 \leq (x + y) \leq 12$. More details can be found in the Computational Methods section of the Supporting Information.

We start our discussion with 2D silicon. Only a single silicene phase has been predicted and synthesized so far, that is, the semimetallic xene phase with a significant conductivity.^{7,8,11} Figure 1a illustrates the most stable structures and convex hull. The most stable pure Si phase in the 2D limit turns out to be a [111] cleaved and reconstructed four-layer FCC bulk Si.³² Expectedly, a four-layer BCC Li slab cleaved in the direction [110] is found to be the most stable pure Li phase³³ in the 2D limit (rightmost) with cohesive energy of -1.56 eV/atom. In comparison, the bulk BCC Li possesses a cohesive energy of -1.6 eV/atom. Similar Li slabs are found in the rightmost bottom position of the hull for all other systems. The most stable structures until $\text{Li}/(\text{Si} + \text{Li}) = 0.5$ are all Li intercalated bulk Si with different cuts, and beyond that point, the most stable systems are Li–Si alloys. However, at $\text{Li}/(\text{Si} + \text{Li}) = 0.5$, lithiated silicene is found to be sitting only 0.05 eV/atom above the globally most stable phase and thus promises to be a favorable anode material thermodynamically. Figure 2a depicts the reported silicene phase and its most stable lithiated counterpart found in our search, along with the energetics and calculated corresponding specific capacity. Next, we perform an AIRSS-based top-down study to find the precise lithiated phase with the same Li concentration and lowest total energy based on the promise it shows. AIRSS is extensively used to study cation binding in monolayers and has been able to reproduce real-life phenomena like electroplating and bond cleavage in the substrate.^{14,15,27,34} To our surprise, we find the undistorted uniformly Li adsorbed silicene highlighted by the evolutionary search to be the most stable phase using AIRSS, too (Figure 3a). This suggests that with a thermodynamically stable lithiated phase and a corresponding high predicted capacity of 954.11 mAh/g silicene is indeed an excellent choice for LIB anode as noted by other recent studies as well.³⁵

Al is the only element in our list whose 2D form has not been synthesized yet, despite having a host of predicted metallic phases.^{28,29} However, the examination of aluminene as LIB anode is vital for several reasons besides completeness. Recently, the 2D form of gallium, which sits just below Al in group IIIA, has been successfully synthesized.^{36,37} Moreover, like bulk Si, bulk Al also possesses a high theoretical storage capacity,³⁸ and its 2D form is therefore expected to perform well. Figure 1b depicts the convex hull and associated most stable structures for Li_xAl_y . The leftmost system is a three-layered and [111] cleaved slice of bulk FCC Al.³⁹ The Li–Al structures on the convex hull are all alloys, except one. The most stable structure of the composition space at $\text{Li}/(\text{Al} + \text{Li}) = 0.5$ seems a two-sided Li-adsorbed 2D material. Closer inspection reveals that this is a two-layer [111] slice of bulk Al. Figure 2b shows all the reported 2D Al phases and their most

stable lithiated phases found in the search along with the energetics and estimated capacities. Although the α , γ , and γ_2 phases are estimated to have an extremely high capacity, they are very unstable in terms of formation energy. However, the lithiated β phase with $\text{Li}/(\text{Al} + \text{Li}) = 0.5$ is positioned only 0.08 eV/atom above the hull. Further top-down AIRSS examination on the β phase with the same concentration of Li reveals a phase change of the adsorbent in the most stable structure, shown in Figure 3b with relevant parameters. The substrate turns from a lithiated β -aluminene to a lithiated [111] cleaved two-layer slice of bulk Al, the global minimum predicted by the evolutionary search. Such an incident further highlights the importance of finding the global minimum, even with a relatively smaller degree of freedom. However, because the Li ions are still adsorbed on the surface, it should be relatively easy to continue the charging–discharging cycles for a long time without a significant loss of capacity. At a predicted storage capacity of 993.36 mAh/g, the metallic β -Al/[111]-Al would make an outstanding 2D LIB anode.

Many 2D boron structures have been predicted in the literature, but only four metallic phases have been experimentally synthesized yet.^{4–6,11} The evolutionary search-constructed convex hull along with the most stable structures is depicted in Figure 1c. Because of the high polymorphism of bulk boron and extensive surface reconstruction in the 2D limit, it is difficult to link the most stable pristine 2D-B (leftmost) to a bulk phase. At $\text{Li}/(\text{B} + \text{Li}) = 0.167$, the most stable structure is a Li intercalated bilayer β_{12} borophene. Remarkably, at $\text{Li}/(\text{B} + \text{Li}) = 0.5$, the system at the global minimum turned out to be the Li adsorbed honeycomb borophene. The honeycomb phase is the most unstable borophene in the pristine and freestanding form that has only been synthesized recently on Al [111] substrate. The deficiency of electrons makes this phase highly unstable in the freestanding structure, and it is found that high charge transfer from the Al surface stabilizes the honeycomb phase.^{6,11} Clearly, the same mechanism highly stabilizes the lithiated honeycomb borophene here, with Li atoms adsorbed on both sides transferring about 0.8 electrons to each B atom on average, which is higher than the contribution from the Al [111] surface (0.7 e/B atom). The synthesized four phases of borophene and their most stable lithiated counterparts, along with relevant energy and capacity values found in the search, are shown in Figure 2c. Even during a 2–12-atom-limited evolutionary search, we note that severe deformation in the adsorbent χ_3 , β_{12} , and striped phases have been found in the most stable lithiated structures. It is also interesting to note that, except the striped phase, all other allotropes contain open hexagons or “hexagonal holes”, and these hexagonal sites (on top of the center of the open hexagons) are always the most stable Li adsorption sites, perhaps because of the electron deficiency of the region. It has also been shown that these hexagonal holes stabilize the flat borophene structure up to a specific concentration.⁴⁰ Because all the four phases in their most stable lithiated structures show massive storage capacity with excellent adsorption energy and good formation energy, we test them with top-down AIRSS with a consistent concentration of $\text{Li}/(\text{B} + \text{Li}) = 0.5$. The most stable structures obtained by using this method and their relevant parameters have been shown in Figure 3c–f. We note that, except the honeycomb phase, all other lithiated phases show severe deformation in the adsorbent that is likely to be irreversible and could lead to capacity fading with recurrent charging–

discharging. Admittedly, the Li concentration in these phases represents slight overcharging according to the bottom-up search. Also, the electroplating-like layered Li adsorption could result in an inefficient charge transfer to the electrode, which would further reduce the effective capacity for these phases. Predictably, the undeformed and uniformly adsorbed honeycomb phase, already established as the global minimum in the previous search, prevails as the most stable phase in this top-down process, too. The striped phase has been demonstrated to possess an extremely low Li diffusion barrier in one direction, resulting in a highly anisotropic Li diffusion.⁴¹ However, with our top-down search, we find severe deformation in the adsorbent that would change the Li diffusion barriers, suggesting the anisotropic diffusion property is likely to be destroyed in a realistic environment. Also, the striped phase is the only synthesized phase without hexagonal holes in it. In the AIRSS-found most stable lithiated phase, we observe partial phase change to the honeycomb phase and opening up of hexagonal holes as highlighted in Figure S4, suggesting a maneuver toward the global minimum. In summary, although the formation energy-based predicted storage capacity of various borophene phases turn out to be less than the uniform adsorption-based predictions,^{11,17} the allotropes can still exhibit an ultrahigh capacity because of their lightness and would make exceptional LIB anodes with their metallic conductivity.

Next, we turn our attention to phosphorus. So far, more than 15 allotropes of 2D phosphorus have been predicted, but only two have been experimentally synthesized: black and blue phosphorene.^{9–11} Both of these phases are predicted to be semiconductors with a semilocal DFT band gap of 0.9–1.9 eV and thus are less suitable as anode materials because of the low electrical conductivity. Figure S1a depicts the evolutionary search constructed convex hull for Li_xP_y . The most stable pristine P phase in the 2D limit (leftmost) turned out to be a bilayer blue-P. The structures situated on the hull, including the most stable phase of Li_xP_y , are all Li–P alloyed systems, which indicates phosphorene is a thermodynamically unsuitable candidate for LIB anodes, as overcharging a 2D-P anode would lead the system to one of these alloyed states. Because of stronger Li–P bonding, the delithiation would be difficult, and the anode most likely would disintegrate after the delithiation. Figure S2a shows the two reported phosphorene phases and their most stable lithiated phases found in our search along with all the energetics and estimated storage capacities. We find that both side adsorption in black-P with $\text{Li}/(\text{P} + \text{Li}) = 0.33$ completely disintegrates the structure, but the single-sided adsorption at the same Li concentration does not. While the black-P fails disappointingly in terms of formation energy, the blue counterpart shows a doubling of storage capacity with a slightly more stable phase. Therefore, we re-examine the lithiation of the blue-P phase with top-down AIRSS algorithm. The most stable lithiated phase of blue-P, shown in Figure S3 with relevant parameters, turned out to be an extremely deformed amorphous-like structure that is energetically far more stable than the uniformly adsorbed phase found in the evolutionary search. This suggests phosphorene phases ultimately would be a poor choice for LIB anode, as hinted by the hull.

Though pristine graphene is already known to be an unsuitable candidate for electrode material, we have included it in our study for completeness. A plethora of phases have been predicted for 2D carbon, but only a handful have been

successfully synthesized so far. Graphene is the most stable and dominant among them.^{3,11} The evolutionary algorithm-found formation energy versus Li–C composition ratio has been shown in Figure S1b. Technically, this cannot be called a “convex hull” because the poor formation of Li–C compounds leads to a rather straight line between the pure C and pure Li phases. The pristine most stable C phase in the 2D limit is bilayer graphene, which is more stable than the monolayer because of the interlayer van der Waals interaction. All phases close to the “hull” turned out to be Li–C alloys. Because we have limited each structure to 2–12 atoms due to the computational budget, large 2D carbon networks such as graphyne and graphdiyne could not be captured in this exercise.¹¹ The pristine graphene (honeycomb) phase and its lithiated most stable counterpart found in the evolutionary search are depicted in Figure S2b. This is a sparsely Li-adsorbed graphene phase with extraordinarily high and positive formation energy that implies a high probability of Li clustering rather than adsorption, reaffirming that the Li storage capacity of pristine graphene is zero.¹¹

To examine the promising AIRSS-found phases’ thermal stability, namely lithiated Si-xene, Al- β , B- χ_3 , B- β_{12} , B-striped, and B-honeycomb, they have been exposed to 400 K temperature through a 10 ps long AIMD run. However, no significant further structural distortion has been observed in any structures, except for some normal Li diffusion, confirming these structures’ thermal stability. The snapshot of the phases is depicted in Figure S5.

The main aim of this study is to thermodynamically deduce the realistic Li-ion storage capacity of various 2D polymorphs of the light elements. Another extremely important figure of merit for prospective LIB anode materials is the diffusion barrier heights for Li ions, which ultimately decides how fast the anode can be charged. Determination of this requires extensive nudged-elastic-band (NEB) calculations or long-time-scale AIMD simulations¹² that are unsuitable for a high-throughput study like ours. Moreover, for distinct adsorbed Li concentrations, the barrier height is expected to be significantly different. Therefore, despite having inspected the Li storage of the discussed polymorphs thoroughly, we are unable to comment on the diffusion barrier heights. However, the diffusion barriers for a single Li ion, which has been accepted as a somewhat reasonable FOM,¹² for most of these materials have already been reported.^{11,17}

In summary, by using a combination of a bottom-up evolutionary structure-searching and a top-down random structure-searching algorithm, we assess the thermodynamic suitability of promising mono-elemental 2D materials as LIB anodes. An energetics-driven prediction of the reversible Li storage capacity for the mono-elemental polymorphs has been made, which is expected to be much more accurate than the uniform-adsorption-based predictions. Locating the global minima of the lithiated compounds guarantees the reliability of these predictions. Multiple instances of movement of a lithiated allotrope toward the global energy minima have been directly observed. Such a lithiation-driven phase change of mono-elemental 2D material toward a more stable phase cannot be captured by using the conventional uniform-adsorption model. Moreover, the inherent polymorphism of the 2D mono-elemental materials might result in synthesis of mixed-phased samples instead of purely single-phased samples.^{42,43} Even for these complex cases, our methodology should be equally efficient and accurate in predicting the

energy-warranted fundamental limit of Li storage capacity. Thus, our study could act as an energetics-driven map for experimentalists in the quest for developing high-capacity Li-ion batteries using mono-elemental 2D materials.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c03642>.

Convex hull of 2D Li–P and Li–C systems, reported phases and their most stable lithiated phases along with relevant parameters for phosphorene and graphene, AIRSS-found most stable 2D LiP phase with appropriate parameters, the partial phase change of lithiated striped borophene, AIMD snapshots of AIRSS-found critical phases, computational methods and supporting references (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Santanu Mahapatra – Nano-Scale Device Research Laboratory, Department of Electronic Systems Engineering, Indian Institute of Science (IISc) Bangalore, Bangalore 560012, India; orcid.org/0000-0003-1112-8109; Email: santanu@iisc.ac.in

Authors

Arnab Kabiraj – Nano-Scale Device Research Laboratory, Department of Electronic Systems Engineering, Indian Institute of Science (IISc) Bangalore, Bangalore 560012, India; orcid.org/0000-0002-7063-0169

Aninda J. Bhattacharyya – Solid State and Structural Chemistry Unit, Indian Institute of Science (IISc) Bangalore, Bangalore 560012, India; orcid.org/0000-0002-0736-0004

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c03642>

Author Contributions

A.K. performed the DFT calculations and the structure searches and analyzed the results. A.J.B. enriched the research aim with experimental insights. S.M. conceived the problem statement and overall supervised the work. All authors contributed to the writing.

Notes

The authors declare no competing financial interest.

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