Graphite plays a critical role in the field of energy storage as the dominant anode material for commercial lithium ion batteries. Such strong commercial success is due principally to its high theoretical lithium capacity (372 mAh g\(^{-1}\) at LiC\(_6\)), high coulombic efficiency, cheap cost, and low intercalation potential.\(^1\)\(^-\)\(^4\)

During the lithium intercalation process, graphite is known to undergo multistage phase transitions with the final transition being from the stage 2 configuration LiC\(_{12}\) (lithium in every other graphite layer) to the stage 1 configuration LiC\(_6\) (lithium in every layer).\(^1\)\(^-\)\(^3\),\(^5\)\(^-\)\(^8\) The average voltage, \(V_{\text{ave}}\), vs lithium metal at which the intercalation occurs is given by Equation 1, where \(e\) is the charge of an electron, \(\mu(y)\) is the chemical potential of species \(y\), and \(x\) is the amount of lithium per C\(_6\) unit cell.

\[
-eV_{\text{ave}}(x_{\text{final}}, x_{\text{initial}}) = \mu(LiC_{x_{\text{final}}}) - \mu(LiC_{x_{\text{initial}}}) + (x_{\text{final}} - x_{\text{initial}})\mu(Li) \tag{1}
\]

If during electrochemical cycling this intercalation potential becomes negative, it will be lower in energy for the lithium ions to plate the graphite rather than intercalate into it. This lithium plating is known to both damage the active material/solid electrolyte interface (SEI) and enable the dendrite formation that can cause significant safety concerns.\(^9\)\(^-\)\(^12\) Such plating can occur as a result of charging graphite beyond LiC\(_{12}\), operating at low temperatures,\(^12\) or charging at excessively fast rates.\(^5\)\(^-\)\(^6\) Adoption of higher voltage anode materials, such as LTO, have enabled batteries with faster charging, but they are inherently accompanied by significant decreases in the full cell energy density.

Analogous definitions to Equation 1 can be taken for all the alkali metals. The ability to intercalate sodium is of particular interest as the development of sodium ion batteries needs a commercially realizable anode material. Interestingly, potassium, as well as the heavier alkali metals (rubidium and cesium), are all known to intercalate into graphite at a stage 1 theoretical capacity of up to 279 mAh g\(^{-1}\) or M\(_4\)C\(_{6}\) (M = K, Rb, Cs).\(^1\)\(^-\)\(^3\),\(^13\)\(^-\)\(^15\) However, sodium is not known to stably form either of the stage 1 intercalation structures, NaC\(_6\) or NaN\(_4\)C\(_6\), at room temperature and ambient pressure.\(^2\)\(^-\)\(^4\),\(^16\)

Ab-initio studies correctly predict this behavior, as the computationally determined values for stage 1 intercalation potentials of both lithium and sodium are positive, whereas sodium is negative.\(^6\)\(^-\)\(^8\)\(^,\)\(^13\)\(^-\)\(^15\) Hence sodium plating, rather than intercalation, is expected. Liu et al.\(^17\) showed that the exclusion of sodium from the alkali metals that can intercalate graphite is a quantitative effect resulting from a balance of ionization energy, which favors the heavier metals, and the metal-graphite interaction, which favors lithium. The net result is that sodium is the only alkali metal with a negative intercalation potential.

In this paper, we demonstrate by density functional theory (DFT) simulation that acceptor doping can increase the intercalation voltages of lithium as well as sodium into the graphite, which is further connected quantitatively with higher rate capability of graphite in lithium ion batteries as well as sodium graphite anodes that can reach stage 1 intercalations. Specifically, we derive the formalism needed to understand how the maximum charging current that a battery can sustain without experiencing lithium plating is directly related to the lithium potential of the anode. We further suggest that by using carbon-site doping to change the intercalation potential of graphite, the maximum charging current can be controlled. This requires a trade-off between power and energy density. Adopting a high-voltage (e.g., acceptor doped) graphite improves the maximum current, and hence power, but reduces voltage contrast with the high-voltage cathode (energy).

Conversely, donor doping should lower the voltage of the anode, which increases the voltage contrast and decreases the maximum charging rate.

Boron and nitrogen are computationally studied here as substitu- tional acceptor and donor dopant examples, respectively. There is a particular interest in boron doped graphite, as previous experimental results suggest that boron can be doped into graphite at a wide range of concentrations and that such doping leads to an increase in lithium intercalation voltage, in agreement with our calculation and theory.\(^18\)\(^-\)\(^29\) For example, experiments have shown that boron can be doped into graphite from low concentrations around 0–3 at%\(^,\)\(^18\),\(^23\)\(^-\)\(^28\) to high concentration of 25–50 at% without loss of the graphite structure.\(^9\),\(^21\),\(^29\) In the case of very high concentrations, Studie et al.\(^21\) showed that the boron concentration in direct synthesis can be continuously varied up until 25 at% without the formation of carbide and that boron doping is accompanied by increased capacity/voltage. 50 at% boron doped graphite requires the presence of lithium, which cannot be completely deintercalated.\(^29\)

Density functional theory calculations were performed to study the impact of carbon site doping on alkali metal intercalation behavior into graphite compounds. Substitutional boron doping was shown to effectively increase the intercalation potential of graphite versus both lithium and sodium metal anodes. The reduced graphite Fermi level of boron doped graphite was shifted away from the \(\pi^*\) antibonding domain toward the more stable \(\pi\) bonds, hence lowering the reduction potential and improving the formation energy for the intercalated graphite. It was further discussed how such methods could be used to improve the intrinsic rate capability of graphite anodes in lithium ion batteries and also enable the use of graphite anodes in sodium ion batteries. We derive an expression representing the transition between thermodynamically favorable intercalation and kinetically favorable metal plating in terms of the applied current. For currents below this transition level, plating should be minimal. This transition point is shown to grow with intercalation voltage, hence higher current capability in acceptor doped systems.
Here we construct a formalism to derive an expression for the onset of lithium plating in terms of both thermodynamics (voltage) and kinetics (current). In other words, for a given state-of-charge, represented by voltage, determine what is the maximum current that can be applied such that plating of the anode is negligible. This expression will determine the current rate at which the system transitions from thermodynamically to kinetically dominated.

This non-equilibrium process is modeled here as a competition between two alternative reaction mechanisms at the graphite anode. The first, Equation 2, is the desired intercalation of a lithium ion in graphite. Equation 3 is the unintended lithium metal plating reaction.

\[ \text{Li}^+ + e^- + C_6 \rightarrow \text{LiC}_6 \]  

\[ \text{Li}^+ + e^- + C_6 \leftrightarrow \text{Li} \ (m) + C_6 \]  

To understand the impact of charge rate on Equations 2 and 3, the electrochemical kinetics are considered. The current with which Equations 2 and 3 proceed are defined in terms of the over potential \( \eta \) (Equation 4), symmetry factors \( \alpha \), and thermal energy \( (k_B T) \):

\[ i^{(i)} = i_0^{(i)} \exp \left( -\frac{\alpha^{(i)} \eta^{(i)}}{k_B T} \right) - \exp \left( \frac{1 - \alpha^{(i)} \eta^{(i)}}{k_B T} \right) \]  

\[ e^{(i)} = \mu \ (\text{LiC}_6) - \mu \ (C_6) - \mu \ (\text{Li}^+) - \mu \ (e^-) \]  

\[ i^{(p)} = i_0^{(p)} \exp \left( -\frac{\alpha^{(p)} \eta^{(p)}}{k_B T} \right) - \exp \left( \frac{1 - \alpha^{(p)} \eta^{(p)}}{k_B T} \right) \]  

\[ e^{(p)} = \mu \ (\text{Li}) - \mu \ (\text{Li}^+) - \mu \ (e^-) \]  

where superscripts \( i, p \) denote the intercalation and plating reactions, respectively.

In the fast charging regime, the full Butler-Volmer reduces to the Tafel equation as \( \eta \ll 0 \). Combining this with the approximation that both reaction mechanisms are relatively symmetric (i.e., \( \alpha^{(i)} \approx \alpha^{(p)} \approx 1/2 \)), the ratio of plating to intercalation current is given by Equation 6 in terms of the intercalation potential (Equation 1). Combining Equations 1, 4, and 5 gives \( V_{\text{int}} = \eta^{(i)} - \eta^{(p)} = [\mu (\text{LiC}_6) - \mu (C_6) - \mu (\text{Li}^+)]/e \), which allows the ratio of the plating to intercalation currents to be presented as Equation 6:

\[ \frac{i^{(p)}}{i^{(i)}} = \frac{i_0^{(p)}}{i_0^{(i)}} \exp \left( \frac{e (\eta^{(i)} - \eta^{(p)})}{2k_B T} \right) = \frac{i_0^{(p)}}{i_0^{(i)}} \exp \left( -\frac{e V_{\text{int}}}{2k_B T} \right) \]  

In contrast to Equation 1, which is a strictly thermodynamic relation indicating which of the two reactions is energetically favorable, Equation 6 recover thermodynamic expectations for plating in terms of the intercalation potential. At \( V_{\text{int}} \gg 0 \) the plating current is near zero, whereas plating dominates at \( V \ll 0 \).

### Accounting for resistance.

The ohmic losses of this system occur in three ways: (i) the lithium ion moving through electrolyte, (ii) the electron moving through the electrode solid matrix, and (iii) the lithium cation moving through the graphite particle (denoted \( \text{Li}^+ \) to \( \text{C}_6 \) to distinguish it from lithium cations moving in the electrolyte - \( \text{Li}^+ \)). Assuming that the third is the dominant form of ohmic losses, the chemical potential becomes \( \mu \ (\text{LiC}_6)_{\text{chrono}} = \mu \ (\text{Li}^+ \text{C}_6)_{\text{chrono}} + e i (\rho_l l) \) where \( i, \rho_l, l \) are the current density through the graphite particle, the resistivity experienced by lithium cations travelling through the graphite prior to reaching the final \( \text{LiC}_6 \) configuration, and characteristic length of the graphite particles, respectively. In this case, Equation 6 becomes:

\[ \frac{i^{(p)}}{i^{(i)}} = \frac{i_0^{(p)}}{i_0^{(i)}} \exp \left( -\frac{e V_{\text{int}} - i \rho_l l}{2k_B T} \right) \]  

The limit of \( i^{(p)} \rightarrow 0 \) occurs in the case of \( V_{\text{int}} - i \rho_l l \gg 0 \). In other words, to minimize plating, the current must be kept below the characteristic current of the particle.

Finally, the ionic resistivity of the graphite can be expressed in terms of a migration barrier \( (E_b) \) and pre-exponential factor \( (\rho_l^0) \) as \( \rho_l = \rho_l^0 \exp(E_b/k_B T) \) leading to an expression for the characteristic current in terms of the computationally determinable variables \( V_{\text{int}} \), and \( E_b \).

\[ i \ll i_{\text{characteristic}} = \frac{V_{\text{int}}}{\rho_l^0} \exp \left( -\frac{E_b}{k_B T} \right) \]  

The limiting equations of Equation 9 reduce to intuitive behaviors. When the voltage is high (e.g., low lithium concentration), plating is dominated by the migration barrier. In this case, if the migration barrier is too large, then the ions cannot pass into the particle and instead must plate the surface. Conversely, in the limit that the particle approaches the theoretical maximum capacity, where \( V_{\text{int}} \rightarrow 0 \), the voltage becomes the current limiting factor. Given that there are no sites for the new ions at this low voltage within the graphite, plating must occur.

### Calculations.

— It appears that the most straightforward process for modifying the graphite intercalation potential is to use carbon site acceptor/donor doping to vary the graphite \( \pi \) band occupation and hence control the reduction potential of the graphite. Donor [acceptor] doping is expected to raise [lower] the Fermi energy and hence raise [lower] the reduction potential. To illustrate this, we used density function theory (DFT) to simulate the intercalation of both lithium and sodium into highly doped graphite. Boron and nitrogen were chosen to allow a very high doping concentration without destroying the graphite lattice due to comparable size with carbon. The carbon site doping concentration had a stoichiometry of \( X \), \( C_{6+x} \) \((X = B^C, N^C) \) with \( y = 0 \), 0.5, 1. To confirm extrapolations to the low doping region, \( B, C_{6+y} \) with \( y = 0.083 \) was also calculated in the case of lithium.

### Methods.

All density function theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) with the van der Waals functional vdW-optPBE. All calculations were performed using the projector augmented wave (PAW) method with \( GGA \) with \( C \), \( B \), \( N \), and \( Li \) VASP pseudopotentials. Relaxations and self-consistent field calculations were performed at 1,000 k-points per atom and density of states calculations were performed at 15,000 k-points per atom. A kinetic energy cutoff of 910 eV was used. Electronic occupancy was smeared using a second order Methfessel-Paxton scheme with \( \sigma = 0.01 \) eV. Intrinsic graphite and high dopant concentration \((y = 0, 0.5, 1) \) in \( B, C_{6+y} \) calculations were performed on a \( 2 \times 2 \times 2 \) formula unit supercell. The dopant ordering was found by comparing the DFT ground state energies of all non-equivalent orderings possible on the supercell size given the restriction that each graphite plane had the same concentration of dopant, and the lowest energy ordering (Figures 1b and 1c) was used. For the low concentration boron doping \((y = 0.083) \) in \( B, C_{6+y} \) a \( 3 \times 4 \times 2 \) formula unit supercell was used with the boron atoms in neighboring planes sufficiently far apart as to simulate a solid solution. Nudged elastic band (NEB) calculations for the lithium vacancy migration barriers in \( LiC_6 \) and \( LiBC_3 \) were performed using the known minimum barrier.
Contrasting with lithium migration in the maximum boron doped case considered (BC$_5$), we see that the most significant difference is that one of the C-C bridges becomes a B-C bridge. In this case, the energy of the intermediate migration states is monotonically decreasing throughout the bond. The net result is that the migration path slips into next unoccupied hexagonal site, resulting in a two site/three C-C bridge migration. In the worst case, when the boron atoms are stacked directly on top of each other, the barrier for this pathway is only slightly increased from the intrinsic graphite case at 486 meV, while the barrier is even lower at 466 meV when the boron atoms are not stacked vertically. Moreover, this change in barrier is local to the boron. When extrapolated back to the low boron concentration regime, the lower barrier graphite C-C bonds will form a percolated network within each plane, insuring that the ionic conductivity remains comparable to intrinsic graphite.

**Discussion**

Our calculations suggest a broad approach to engineering doped-graphite battery anodes. The general trend is that hole doping increases alkali metal intercalation potentials whereas electron doping decreases the potential. With minimal structural changes, this variance in the intercalation potential is determined principally by the total occupation of the graphite antibonding $\pi^*$ in the intercalated state. In intrinsic graphite, the only antibonding electron is what accompanies the lithium ion. In the case of boron doping, the hole partially cancels this electron and, for nitrogen doping, the doped electron adds to it. This suggests that by designing the occupation of the $\pi^*$ in the intercalated state, energy density in form of voltage contrast between the anode and cathode can be sacrificed to obtain a high maximum charge current/power density.

Equation 6 indicates that increasing the intercalation voltage of graphite via boron doping can have significant impact on plating current. Here we consider the example of designing graphite to intercalate at 0.36 V vs lithium metal to double the intrinsic intercalation potential of 0.18V as seen in Figure 1a. By doing

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**Figure 1.** (a) Average intercalation potential for lithium (left) and sodium (right) into boron/nitrogen doped graphite between the states of $X_y C_{6-y}$ to $AMX_y C_{6-y}$. (b) and (c) The in-plane dopant ordering for $XC_5$ and $X_{0.5}C_{5.5}$, respectively.
so, we expect the plating to intercalation current ratio to square \((i^{(p)}/i^{(i)})^2\), making the plating more difficult to happen. Since the calculated intercalation potential for lithium intercalation in the boron doped systems are very close to linear in boron concentration (ie. \(V^{(Li)}_{BC} \approx (V^{(Li)}_{B0} + V^{(Li)}_{C5})/2\), we can interpolate that a concentration of approximately 1.5 at% \((B_{0.087}C_{5.913})\) would be sufficient to reach the desired 0.36 V intercalation potential for lithium. To compare, 1.38 at% \((B_{0.083}C_{5.917})\) was calculated and showed an intercalation potential of 0.54V, implying that the impact of doping is in fact super-linear at low concentrations. Accordingly, we just need less than 1.5 at% boron doping to square the current ratio and significantly increase the power density.

Similar to lithium intercalation potential’s dependence on boron concentration, the sodium concentration is also nearly linear.
(\(V_{B_{0.41}C_{5.59}}^{(Na)} \approx (V_{BC5}^{(Na)} + V_{C5}^{(Na)})/2\)). Following the linear interpolation detailed above, we predict that 7 at% of boron \((B_{0.41}C_{5.59})\) would be sufficient to lead to a similar sodium intercalation potential as that of lithium into pristine graphite (0.18 V).

### Conclusions

Graphite remains the most prolific anode material in commercial lithium ion batteries, but its performance in both fast charging lithium ion batteries and in sodium ion batteries leaves much room for improvement. We have computationally determined that carbon site acceptor doping shows promise as a mechanism to improve both of these performance limitations. The outlined kinetic picture tied together how the charging-rate limit of lithium and the charging ability of sodium are related, in both cases experiencing exponential improvement upon increases in the intercalation potential. Such increased intercalation potential was shown to be achievable using boron doping, which had negligible impact on graphite inter-layer spacing or diffusivity.

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**References**


