

Article

Sodium Adsorption and Mobility in a Pillared Graphene Structure

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Abstract

Sodium-ion batteries are generally considered a promising alternative to lithium-ion batteries due to the abundance and low cost of sodium. However, their main limitation is the lack of an appropriate anode, since the usual graphite electrode used in lithium batteries is incompatible with the larger ionic radius of sodium. In this work, the theoretical behavior of pillared graphene as a possible anode is analyzed via computational simulations based on Density Functional Theory (DFT) using the FIREBALL program. The structural relaxation results reveal that staggered pillars are more stable than the aligned alternative. The adsorption energy of sodium is shown to be significantly higher than for graphite, with a maximum value of -2.23 eV, leading to an important energetic benefit. The diffusion analysis shows high mobility for sodium, with migration barriers comparable to those of lithium ions both in the flat regions of the structure and close to the nanotubes. The values are comparable to those of the standard graphite used in current batteries. Finally, the charge analysis confirms significant electronic transfer from both sodium and lithium to the lattice. These data indicate that pillared graphene can be a good candidate for the optimization of charge dynamics in sodium-ion batteries.

Keywords: pillared graphene; DFT; charge transfer; Na batteries; energy barrier

1. Introduction

The global energy storage market is dominated almost entirely by lithium-ion batteries, which rely on the reversible intercalation of lithium cations between a cathode and an anode. Despite their high energy density, lithium-ion batteries face a series of sustainability and supply chain constraints. The primary issue is the scarcity of lithium; there is a limited number of deposits, which are located in geopolitically complex areas [1]—mainly in South American countries such as Chile, Bolivia, and Argentina, collectively known as the lithium triangle. Lithium production is also restricted to a few countries [2], predominantly China. Furthermore, mineral extraction is expensive, both economically and environmentally [3], as it consumes massive volumes of water and generates toxic pollutants. The use of batteries itself can be hazardous given their tendency to combust under certain conditions due to thermal runaway [4]. Adding to this, their recycling is complex and is not practiced on a large scale [5]. Finally, lithium is not the only problematic element in these batteries, since one of the most common cathodes is composed of LiCoO_2 , and cobalt is even more scarce than lithium [6]. All these factors complicate the production of these types of batteries.

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Sodium-ion batteries offer a promising alternative due to the abundance of sodium in seawater and halite ores, alongside its favorable charge transport properties [7]. Moreover, sodium batteries do not require cobalt cathodes [8,9], mitigating supply chain vulnerabilities and reducing the projected production costs [10].

However, an important problem in the development of sodium-ion batteries is the lack of suitable anode materials. While graphite serves as an efficient host for lithium, sodium intercalation into graphite has been shown to be thermodynamically unstable [11] due to insufficient interlayer spacing. Previous theoretical simulations based on Density Functional Theory (DFT) have studied the adsorption and mobility of Na atoms intercalated in graphite, providing an explanation for this incompatibility [11,12]. Therefore, the design of low-cost, structurally optimized anodes capable of efficient sodium storage is necessary.

Carbon nanomaterials are ideal candidates for this purpose due to their abundance, high electrical conductivity, low weight, and structural tunability. The main contender as a promising electrode for future Na-ion batteries is currently hard carbon [13–17], which, despite yielding promising results, still has considerable room for improvement [18]. Several approaches have been explored to modify graphite-based materials, including mechanical treatments such as ball milling, mild oxidation, and heteroatom doping [19]. Experimentally, these strategies are known to introduce defects, vacancies, oxygen-containing functional groups, and local structural distortions, which strongly affect the interaction of alkali ions with graphitic carbon [20,21]. Recent first-principles studies have further revealed that vacancy defects and heteroatom dopants can enhance Na adsorption and modify diffusion pathways by altering the local electronic structure of graphene [22–24].

An alternative option is expanded graphite, in which the interlayer spacing is increased using functional groups [25,26] or other structural protuberances [27]. Experimental results demonstrate that it can yield a significantly higher capacity than standard graphite and retain it over many charge-and-discharge cycles. Unfortunately, the functional groups repel the Na ions, reducing the storage density. Additional works have analyzed expanded graphite using alternative methods [28,29]. Furthermore, other theoretical works have studied the most favorable interlayer distance for Na intercalation [30].

Following this idea, recent works have explored the possibility of expanding the graphene–graphene interlayer distance using carbon nanotubes (CNTs). Such structures, termed *pillared graphene*, have been primarily investigated in the context of hydrogen storage [31–33], but the idea can be easily extended and applied to anodes built with graphite-like materials, where the increased interlayer distance could allow greater Na mobility. The elasticity of this compound has been studied before, and it could prove to be an important parameter to take into account for both molecular storage and the electrodes of batteries [34,35]. Due to the difficulties in creating such a structure, it is prudent to perform theoretical simulations to test the viability of the structure for future application as an anode in Na-ion batteries. Nevertheless, motivated by the initial theoretical works, some efforts have been made to synthesize pillared graphene experimentally [36].

In this work, we employ DFT simulations to investigate the adsorption energy and mobility of Na atoms within a purely carbon framework. This structure utilizes CNTs as structural pillars to expand the interlayer distance of graphite-like sheets, with the CNT bonded to both adjacent graphene layers. CNTs were chosen for their affinity with sodium [37] and their large number of geometric degrees of freedom, allowing for tuning of the height, chirality, and diameter. We analyze the stability of aligned and staggered structures; study the adsorption energy at various points throughout the structure to determine migration barriers for one, two, and three atoms; and, finally, evaluate the charge transfer between Na and the C-structure. Throughout this process, the results for Na were compared with those for a Li atom in the same structure and for both Na and Li in a regular

graphite structure. The results indicate that the material is a promising structure for a future anode in Na-ion batteries.

2. Materials and Methods

A highly efficient DFT localized orbital molecular dynamics technique (FIREBALL [38]) is used for the structural relaxation of all systems involved in this study. The computational scheme has been described in full elsewhere [38–40]; therefore, only the main points are summarized here. The code is based on a self-consistent version of the Harris-Foulkes functional [41,42]. The FIREBALL simulation package uses a localized atomic orbital-like basis [43] that reaches zero for a certain cutoff radius, drastically reducing the number of interactions to be computed during the relaxation process. Norm-conserving pseudopotentials are calculated using the Troullier–Martins methodology [44] with the tool included in the FIREBALL package [38]. In the present work, the cutoff radii for the wavefunctions' radial part defining the optimized basis set are the following: $r_s = 4.5$ for the Na atom, $r_s, r_p = 4.5$ for the C atom, and $r_s = 4.0$ for the Li atom. Different C-based compounds (graphene, graphite, and CNTs) have been successfully characterized both electronically and structurally in previous works using this code [45–47]. In particular, in the graphene case, the C–C distance is 1.425 Å, which is very similar to the experimental value of 1.42 Å [48]. Furthermore, the density of states accurately describes the expected behavior of graphene, as presented in [45]. On the other hand, the cutoff radius chosen for the Na atom has been used satisfactorily to reproduce its ionic behavior in previous works [49]. Finally, as lithium presents a shorter ionic radius than sodium, we accordingly select a shorter cutoff radius. It is important to note that the confinement imposed by finite cutoff radii affects the absolute values of the calculated energies. Consequently, the present calculations are expected to yield more reliable qualitative trends than quantitatively accurate energetic predictions. In addition, the code uses the local density approximation (LDA) exchange–correlation functional calculated with the multi-center weighted exchange–correlation density approximation (McWEDA) [40], and self-consistency is achieved via the occupation numbers given by the Harris functional [41]. For the charge analysis, we use Löwdin population analysis, as explained in the FIREBALL review [38].

As mentioned in the Introduction, we analyze a carbon-based structure consisting of a graphene sheet joined to a carbon nanotube, which acts as a structural support to increase the interlayer spacing. In our calculation, we include periodicity in the Z-direction to reproduce a graphite-like configuration. It is important to note that the model presents a hole in the graphene sheet in the area where the CNT is bonded. To determine the type of nanotube, the size of the graphene sheet, and their relative orientation, we use the results obtained by Yang et al. [50], where a (6, 0) zig-zag nanotube joined to a 10×10 armchair graphene sheet (which will henceforth be called ARM-60) was found to be the best option. In Figure 1a, the structure of the CNT bonded to the graphene sheet is shown. The lines represent the unit cell, meaning that the CNT of the consecutive unit cell in the Z-direction is aligned with the one presented in the figure. On the other hand, Figure 1b shows a tilted unit cell that leads to a configuration with staggered CNTs. Finally, Figure 1c reflects the junction between the graphene layer and the CNT (see the heptagon formed due to the bonding of the C atoms coming from both the graphene and CNT). This structure was previously proposed as the best candidate for electrical conductivity [50]. Due to the large size of the system proposed, the calculations are performed using only the Gamma point in the first Brillouin zone. Some tests with larger numbers of k-points (2, 8 and 32) have been performed in a hollow site, obtaining energy differences of +0.04, −0.02, and +0.01 eV, respectively. Similar differences were found on a neighboring bridge site. Additionally, the atomic configuration remains almost untouched, and the change in charge transfer is

around 0.02 e greater. Consequently, we can conclude that the use of the Gamma point is sufficient for this analysis. The atomic relaxation is considered converged when the maximum force on any atom is less than 0.05 eV/Å and the maximum total energy change is smaller than 1×10^{-4} eV/atom.

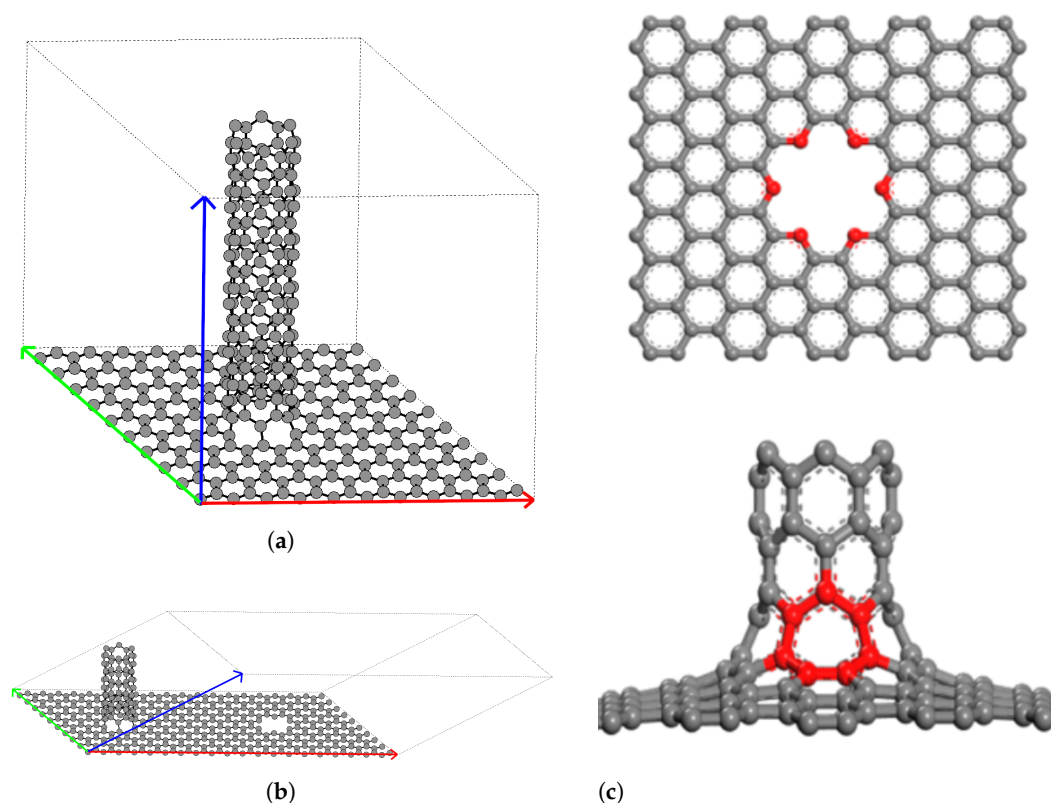


Figure 1. Initial ARM-60 structures aligned (a) and staggered (b), where the colors red, green, and blue correspond to the X, Y, and Z lattice vectors, respectively; (c) shows the junction between the (6, 0) CNT and graphene [50].

We wish to find the optimal configuration after joining the CNT to the graphite-like structure. The first step is to study the alignment of the nanotubes (the aligned and staggered structures can be seen in Figure 1a,b). The separation between the nanotube and graphene is an important point in our analysis. We study the stability of the structures by slowly increasing the separation for both the aligned and staggered structures until a minimum is found (Section 3.1). The size of the nanotubes is also analyzed by changing the length to determine which is optimal. Once we have found the best pillared graphene structure, one sodium or lithium atom is placed in various positions in the structure (Section 3.2). After the relaxation of these structures, we determine the adsorption and migration barriers for both atoms, as well as the charge transfer in all calculated positions (Section 3.3). The adsorption energy (E_{ads}) is estimated by comparing the energy of the system with that of the Na (Li) atom in the pillared graphene structure together (E_{TOT}) and the energy of both subsystems situated far apart, i.e., the energy of the pillared graphene (E_{PGR}) separated from the Na (Li) atom. The latter energy is calculated as the atomic energy in its corresponding bulk structure ($E_{Na(Li)}$).

$$E_{ads} = E_{TOT} - E_{PGR} - E_{Na(Li)} \quad (1)$$

A negative value means that the adsorption is favorable, and a positive value implies a repulsive interaction. All these values are compared with our simulations of the atoms in a graphite structure. In particular, the reference graphite calculations consist of a

6×6 graphene unit cell sampled with 256 k-points, with the red atom placed in the center in both a hollow and bridge position. The graphite calculation uses an interlayer distance of 3.4 (the natural interlayer distance of graphite in FIREBALL), as well as 3.7 Å for Li [51] and 4.5 Å for Na [52,53] for comparison with other theoretical works. A comparison is also established with previous theoretical data when appropriate [12].

Finally, a note on the methodology is warranted. Although the LDA approach lacks the nonlocal correlation required to accurately describe long-range van der Waals (vdW) interactions, it is well known to overestimate binding in systems where dispersion forces are important. This spurious overbinding can partially compensate for the missing dispersion contribution, often resulting in reasonable structural properties due to error cancellation. Furthermore, the graphene–graphene distance is fixed by the strong interaction with the CNT. Consequently, the vdW interaction should not affect the geometry of the structure. Additionally, the vdW interaction is compensated for in the adsorption energy calculation, thus having a minimal impact on this part of the analysis. Finally, the Na–graphene interaction is dominated by a more intense electrostatic interaction established due to charge donation. For all these reasons, the vdW interaction is not taken into account in this work. However, it is acknowledged that the absolute adsorption energies and migration pathways may shift under dispersion-inclusive functionals. This vdW effect, along with the uncertainty added by the localized orbital parameters and the LDA approach used in FIREBALL, should be evaluated in future calculations using plane-wave codes under better exchange and correlation functionals.

3. Results

3.1. Structural Relaxation

The first step is to determine the most stable structure where the Na and Li atoms can later be placed. The initial configuration has the nanotube (of 11.36 Å in axial length) in close contact with the graphene layer (1.42 Å, reflecting the bond distance in graphene), fixing the periodicity in the Z-direction such that the gap between the upper CNT atoms and the adjacent periodic graphene layer is identical to the bottom contact. Then, we increase the separation by enlarging the corresponding lattice vector. After relaxation, the C atoms next to the hole in the graphene sheet are moved to create bonds with the unsaturated orbitals of the border atoms of the CNT. Repeating this process several times enables us to find not only the most stable configuration but also the general trend in the behavior of the structure under mechanical deformation. These sequential calculations are performed for both the aligned and staggered configurations shown in Figure 1a,b.

Furthermore, as described in the following section, we also vary the length of the nanotube. Consequently, separation is defined as the difference between the periodicity in the Z axis and the length of the nanotube divided by two (given that there are two junctions), which is independent of the axial length of the nanotube.

3.1.1. Alignment

First, we determine which of the aligned or staggered nanotubes is the most stable, as well as the optimal separation between the nanotube and the graphene layer. Figure 2 shows the energies of both structures as a function of the separation defined previously. As can be observed, the staggered structure is more stable, with its most stable configuration at 3.7 Å of separation. This apparently large distance can be understood by taking into account the atomic configuration shown in Figure 3b. Due to its great elasticity, the graphene layer presents buckling in the original planar structure. The C atoms bonded to the CNT move up (or down depending on the position of the CNT above or below the hole) by around 2.25 Å. Adding the original distance of 1.42 Å between the CNT and the graphene, we

have almost the distance defined. It is important to note that, while the graphene layer is strongly deformed, the CNT is only stretched by around 0.1 Å, reaching the total of 3.7 Å in Figure 1b. This situation leads to a large graphene–graphene distance of 18.7 Å, which allows for Na intercalation.

Vertical relaxation of the structures

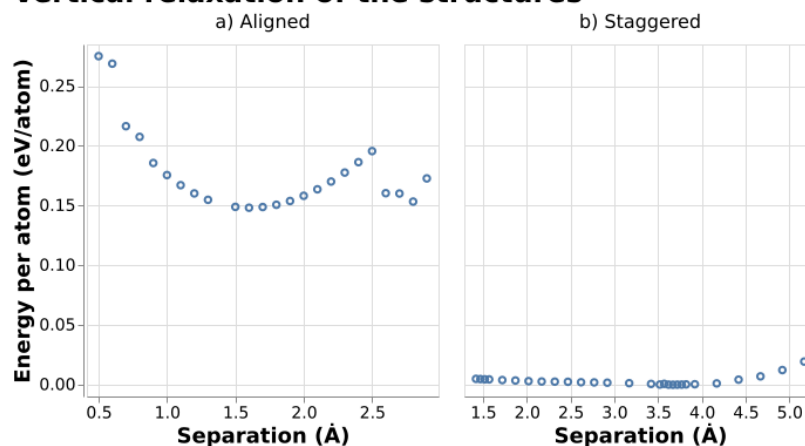


Figure 2. Energy per atom of (a) aligned and (b) staggered ARM-60 structures during the stretching process. Energy reference set to the minimum value of the staggered structure. Separation is measured as the periodicity on the Z axis minus the length of the nanotube divided by two.

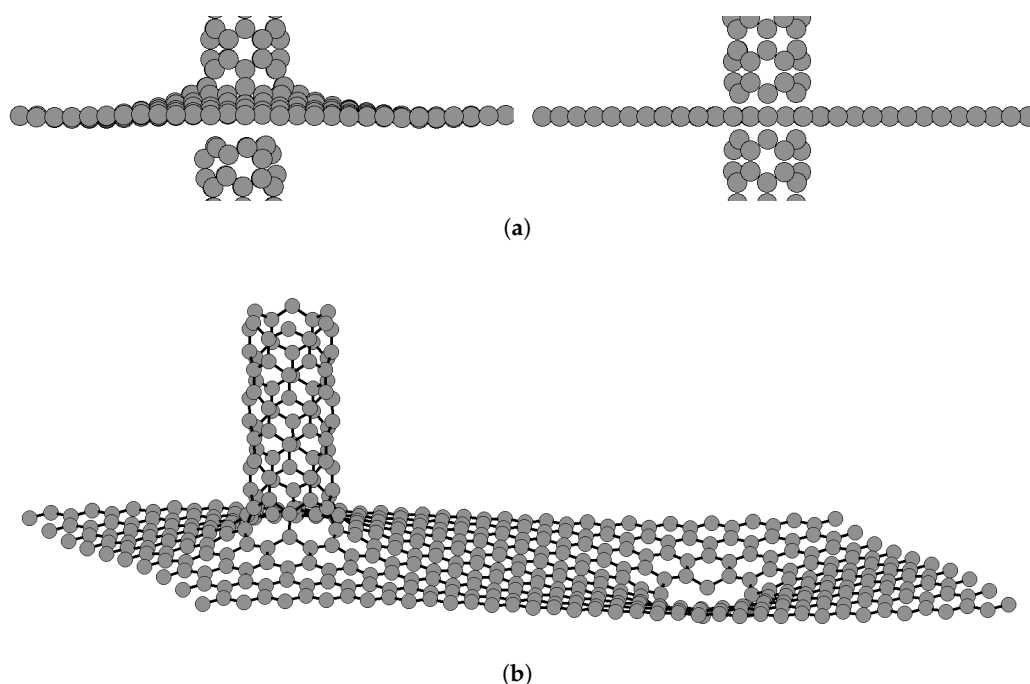


Figure 3. Structures in Figure 1 after relaxation, (a) presents two panels: on the left, the CNT is disconnected from the upper CNT; on the right, the upper part of the first CNT is connected to the graphene layer. (b) shows the most stable staggered ARM-60 structure after relaxation.

Notably, the aligned structure tends to “break” (the broken structure can be seen in Figure 3a) when stretched beyond a critical point, which explains the sudden energy jump at the end of the graph. This behavior is consistent with the results in [50], since the stability of the ARM-60 structure is due to the relatively stable heptagon formed in the junction (as shown in Figure 1c). The aligned case implies the bonding of each graphene sheet with two nanotubes (above and below); then, it cannot form these very stable bonds with at least one of the sides. As a consequence, the system tends to favor the formation of

these bonds with only one of the two nanotubes over maintaining symmetry at higher separations. In contrast, the staggered structure (which can freely form these very stable bonds at both junctions) suffers a very small energetic variation as the separation increases, indicating greater resistance to mechanical deformation. This result is consistent with previous works [34,35] and is favorable regarding its use as an electrode working under different stress conditions.

Given that the staggered structure is more stable, all subsequent analyses are performed with the staggered configuration.

3.1.2. Nanotube Length

The length of the nanotube is an important parameter for a future electrode in Na-ion batteries as it is useful for expanding the interlayer distance, favoring Na adsorption and mobility; however, a large CNT can reduce the number of Na atoms accepted in the anode, reducing the electrical capacity. For this reason, it is important to analyze the variation in the CNT length in order to find the most optimal configuration. Due to the type of CNT selected, the length is constrained by the fact that it must have a zig-zag edge on both ends, since this is required for the formation of the desired junction. Therefore, the length may vary only in increments of three atoms, which implies that length 1 will correspond to 4 atoms (2.84 Å), 2 to 7 (7.1 Å), and 3 to 10 (11.36 Å), where the original version shown in Figure 1b corresponds to length 3.

Figure 4 shows the energetic evolution (energy per C atom) of the ARM-60 staggered structure for three CNT lengths as a function of the separation defined previously. The graph shows that the most stable structure is the one with the shortest nanotube, although the energy difference is relatively small compared to that obtained in the aligned case (see Figure 2). This result can be understood by the fact that the shorter the nanotube, the closer the structure is to graphite, which should be the most stable option.

Vertical relaxation for different nanotube lengths

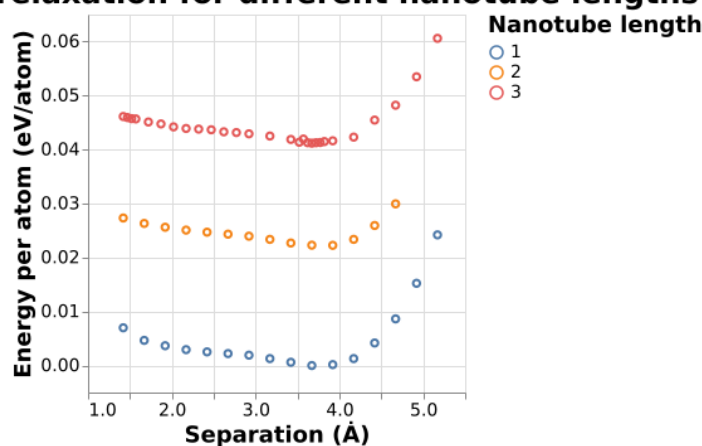


Figure 4. Energy per atom of the staggered ARM-60 structure for different nanotube lengths. Energy reference set to the minimum for the length 1 structure.

It is also clear that the optimal separation for all nanotubes is roughly the same, i.e., around 3.7 Å. This behavior is also expected since the optimal separation is primarily influenced by the interaction between the graphene and nanotube (i.e., the junction), which is independent of the nanotube length.

3.2. Atomic Adsorption and Migration

Once the best structure is determined, it is possible to analyze the adsorption of the Na (Li) atom in different positions in the structure. In particular, we analyze two main types of

being that the moving atom is placed underneath the graphene sheet, whereas the static atom is on top.

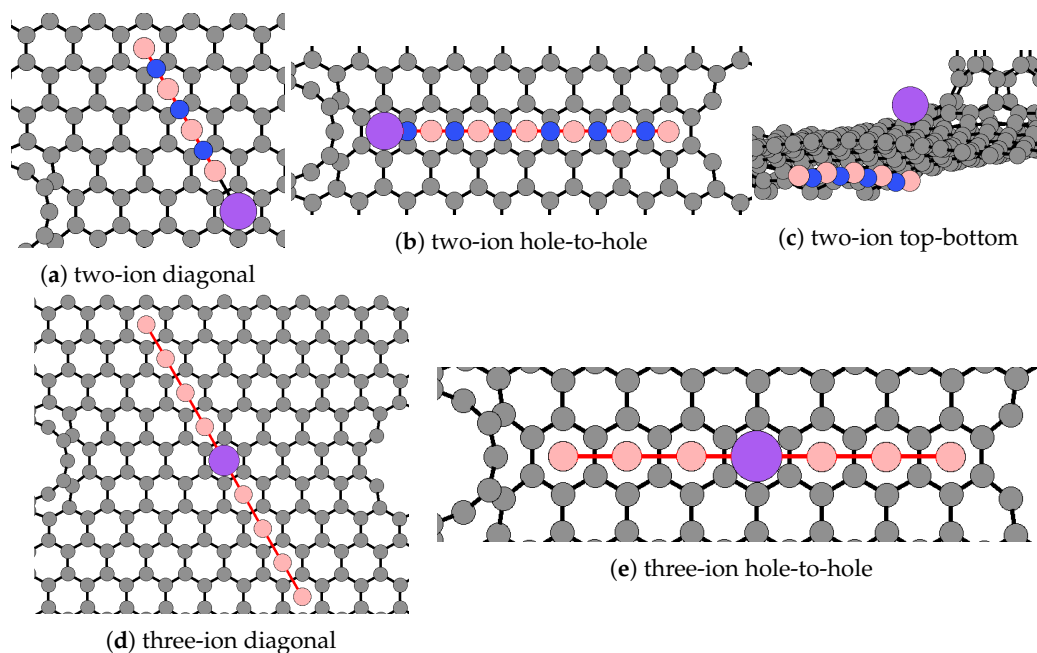


Figure 6. All multiple-atom positions that are studied, divided into their respective paths. Pink (blue) spheres represent hollow (bridge) sites, and large purple spheres represent the static atom. (a) represents steps 0 to 6 from bottom to top. (b) represents steps 0 to 10 from left to right. (c) represents steps 0 to 8 from right to left. (d) represents steps 0 to 4 from closest to the static atom to farthest. (e) represents steps 0 to 3 from closest to the static atom to farthest.

3.2.1. Adsorption and Migration Energies for Sodium vs. Lithium

The primary goal of this work is to demonstrate that Na exhibits similar (or even superior) performance (adsorption and migration energies) to Li within the proposed pillared graphene structure. Figure 7 shows the adsorption energies of all structures calculated with one Na or Li atom on the hollow sites, as well as in the different bridge positions. It is important to note that the different configurations all lead to negative adsorption energies, reflecting the successful accommodation of both Na and Li in the pillared graphene structure. Moreover, it can be observed that, in the worst case (the flat region, hole-to-hole), sodium has an adsorption value of around -0.8 eV in hollow positions, whereas, in the best case (in the middle of the nanotube), it reaches -2.23 eV. On the other hand, the Li atom has the least (hollow) attractive site at -0.62 eV in the hole-to-hole section near the middle, while the most attractive is found at the most extreme point of the nanotube, where it has a value of -1.91 eV. Both elements show a similar trend, with the Na atoms having generally higher adsorption in all three paths. We compare these values with the reference graphite calculations, where we obtained -0.29 eV for Na and -1.64 eV for Li on the hollow sites, demonstrating that pillared graphene significantly outperforms regular graphite in terms of sodium adsorption.

Figure 7 shows that the in-tube path has an irregular distribution of hollows and bridges. This is due to the fact that hollow positions are defined as stable (not requiring the fixing of the coordinates), and, in this case, the only truly stable positions are those in the very middle of the nanotube (in a somewhat symmetric position) and at the extremes; all other positions require the fixing of the coordinates. In comparison, the hole-to-hole and out-tube paths have a more normal distribution of hollows and bridges, with hollows generally having larger adsorption energies than bridge sites.

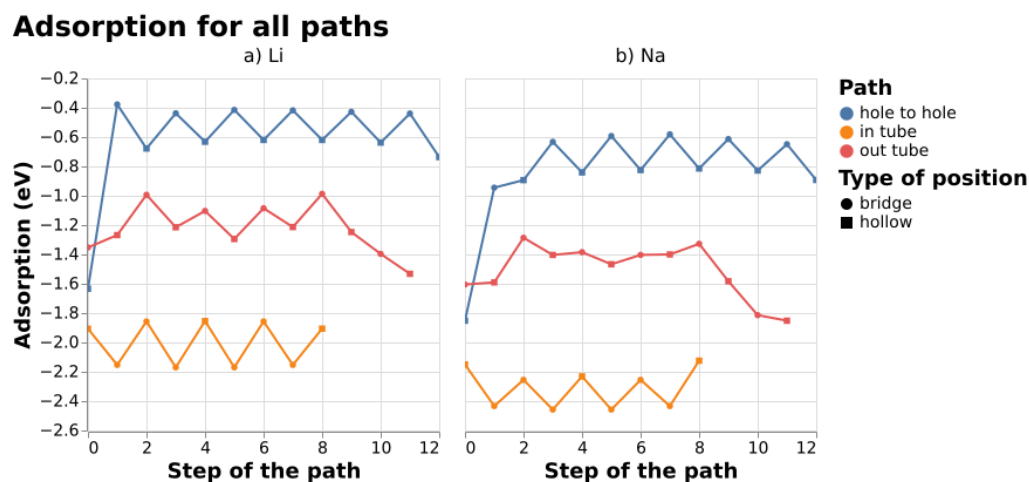


Figure 7. Adsorption energy for the three paths presented in Figure 5 for (a) lithium and (b) sodium in the structure displayed in Figure 3b. In blue, the hole-to-hole case is shown; in red, the within-CNT path is shown; and, in yellow, the movement of the Na/Li atom outside the CNT is shown. Squares and circles correspond to hollow and bridge sites, respectively.

A common behavior for both atoms is that they tend to have larger adsorption near or outside the nanotube. In fact, the highest adsorption (most stable) position for sodium is precisely in the middle of the nanotube, with the extremes closely following. Lithium overall behaves very similarly, although it has slightly higher adsorption outside the nanotube rather than inside. Note that this analysis is performed with a single atom, whereas a real system would likely be saturated with them, in which case ionic repulsion would affect these values. A preliminary multi-atom analysis is provided in the following section.

In Table 1, we list the migration energies, calculated as the difference between the energy in one hollow site and that in the next bridge position, for the three paths. Several interesting findings can be observed. First, in all cases, sodium has lower migration barriers than lithium in and around the CNT, while, on the relatively flat graphene-like region covered by the hole-to-hole path, they have indistinguishable barriers. These values can be compared to the barriers calculated with our reference graphite structure built with a 3.4 Å interlayer distance (1.77 eV for Na and 0.61 eV for lithium). Increasing the interlayer distance to the value that accommodates both atoms in the best way, namely 4.5 Å for Na and 3.7 Å for Li, we obtained reduced barriers of 0.19 eV and 0.28 eV for Na and Li, respectively. It is clear that the increased separation to allow for the intercalation of the atoms in graphite decreases the migration barrier significantly. Comparing these reference values with those of pillared graphene, we can see better performance for Li and comparable performance for Na; the fact that the barriers are slightly higher can be attributed to the curvature of the graphene sheet, which has been shown to increase the migration barriers in previous works [54]. Overall, the increased adsorption and similar (or lower) migration barriers represent a notable improvement for both atoms. Furthermore, comparing Na with Li, in our graphite reference or in pillared graphene, sodium outperforms lithium in all paths. Even when comparing the barriers for Na with the values obtained in other works (~ 0.3 eV in graphite with an interlayer distance of around 4.5 Å [12,52]; ~ 0.15 eV on a graphene surface [52,54]), our theoretical calculations suggest that pillared graphene could compete with graphite in the flat region. This is a promising result, since it seems to permit atomic mobility both horizontally and vertically, allowing the atoms to diffuse throughout the structure. Furthermore, it is likely that, once more Na atoms are introduced into the system, these barriers could decrease. In the best region (the outside of the nanotube), the Na atom shows complex behavior, presenting very similar energies in all sites analyzed at the central part of the CNT, suggesting easy migration in this area. Meanwhile, Figure 7

shows larger barriers when the Na atom approaches the CNT's borders, suggesting the pinning of the Na atoms, which could reduce the atomic mobility.

Table 1. Migration barriers in eV for the paths in Figure 7, calculated as the difference between contiguous positions. Filtered values display the mean and standard deviation with the outlier values removed.

Step	Path Atom Direction	Hole-to-Hole		In-Tube		Out-Tube	
		Li	Na	Li	Na	Li	Na
1	Forward	1.26	0.91	0.30	0.18	0.27	0.30
	Reverse	0.30	0.00	0.31	0.20	0.22	0.12
2	Forward	0.24	0.26	0.32	0.23	0.11	0.02
	Reverse	0.19	0.21	0.32	0.23	0.19	0.08
3	Forward	0.22	0.25	0.31	0.20	0.21	0.06
	Reverse	0.21	0.23	0.30	0.18	0.13	0.00
4	Forward	0.20	0.24	0.25	0.31	0.23	0.07
	Reverse	0.20	0.23	-	-	0.26	0.26
5	Forward	0.19	0.20	-	-	0.00	0.00
	Reverse	0.21	0.21	-	-	0.14	0.04
6	Forward	0.20	0.18	-	-	-	-
	Reverse	0.30	0.24	-	-	-	-
Mean		0.31	0.26	0.30	0.22	0.18	0.10
Std Dev		0.30	0.21	0.02	0.04	0.08	0.10
Filt. Mean		0.22	0.23	0.30	0.22	0.20	0.07
Filt. Std		0.04	0.03	0.02	0.04	0.06	0.08

3.2.2. Multiple Atoms

In this section, we aim to provide some preliminary, qualitative results about the behavior of this system in the presence of multiple atoms. Note that, as the number of atoms increases, the number of possible combinations of positions increases combinatorially, making it computationally prohibitive to analyze all of them. Therefore, we select a few paths focused on the graphene-like area, on which most of the atoms would be located. Nevertheless, these data provide some insight into the general behavior of multiple ions in the structure.

Figure 8 shows a clear trend of higher stability as the atoms grow farther apart, which is expected given the fact that they transfer some of their charge to the lattice and therefore repel each other. It is also clear that the hole-to-hole path remains the most favorable; this is also expected since one of the atoms is placed near the nanotube—in a site with one of the highest adsorption energies throughout the system.

To analyze the effect of repulsion, we examine the energy of the combined system compared to the sum of the energies of the individual systems. For steps at the start of the path (when the atoms are close), the difference is large (−0.83 eV vs. −2.74 eV for Na and −1.24 eV vs. −2.37 eV for Li), meaning that repulsion plays an important role; in fact, Na seems to have a larger effect than Li. On the other hand, when they move farther away, the difference becomes much smaller (−2.28 eV vs. −2.66 eV for Na and −1.85 eV vs. −2.29 eV for Li) and the pattern reverses, where the difference is larger for Li than for Na. This could be because (as seen in Section 3.3.2) Li retains considerably less charge, and, in the region close to the nanotube, the charge is much more localized (80% of the charge is contained in the closest 18 C atoms). These two effects combined could lead to a screening effect for

Li, which can explain why the effect of repulsion appears smaller when they are closer together. Meanwhile, in general, Na has higher adsorption than Li in the structure, but, in the earlier steps, the stronger repulsion effect dominates and thus it performs worse than Li. As the atoms move farther apart, the effect of repulsion decreases and the higher adsorption is again visible.

Adsorption for all paths

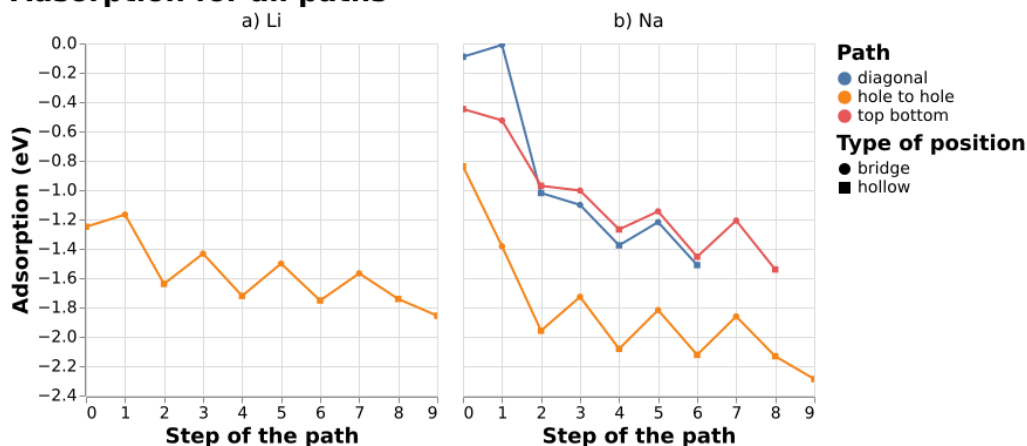


Figure 8. Adsorption energy along (a) path (a) of Figure 6 for Li and (b) paths (a–c) for Na.

Looking at the mean barrier values displayed in Table 2, it may appear that there is no significant difference between the barriers for two atoms compared to one atom; however, the difference becomes clear when examining the barriers for the first two steps. In the first step, there is zero barrier; in the second, the forward barrier is noticeably lower and the reverse barrier is noticeably higher. Therefore, it appears that the presence of a second atom reduces the migration barriers, but only when they are very close to each other; otherwise, it is negligible.

On the other hand, Figure 9 shows an entirely different trend, where step 0 (where the atoms are the closest) is more stable than step 1 but less stable than step 2, and (in the diagonal path) step 3 is less stable than step 2. The reason for this behavior is due to two main factors: the charge transfer (Section 3.3.2) and the distance between the atoms. In the closest position, the atoms cede very little charge, meaning that they do not repel each other significantly. On the other hand, in step 1, they cede more charge, leading to increased repulsion, which explains the lower stability. In step 2, the charge transfer is similar; thus (similarly to the two-atom case), being further away offers greater stability.

Note that the large jump between steps 1 and 2 of the hole-to-hole path is due to the fact that, in this position, two out of the three atoms are in a highly favorable adsorption site, near the nanotube.

3.2.3. Nanotube Length

Next, we perform a similar analysis exclusively for a single Na atom on the hole-to-hole path while varying the length of the nanotube. This is important to test the effect of the interlayer distance with the migration barrier, as we wish to reduce the CNT size as much as possible.

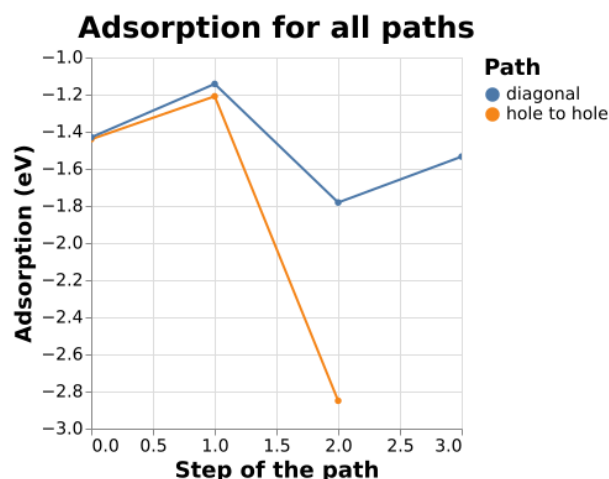


Figure 9. Adsorption energy along paths (d,e) of Figure 6 for Na. All positions are hollow sites.

Table 2. Migration barriers in eV for the paths in Figure 8, calculated as the difference between contiguous positions. Filtered values display the mean and standard deviation with the outlier values removed.

Step	Path Atom Direction	Diagonal	Hole-to-Hole		Top Bottom
		Na	Li	Na	Na
1	Forward	0.08	0.08	0.00	0.00
	Reverse	1.01	0.47	0.58	0.45
2	Forward	0.00	0.21	0.23	0.00
	Reverse	0.28	0.29	0.35	0.26
3	Forward	0.16	0.22	0.26	0.12
	Reverse	0.29	0.25	0.31	0.31
4	Forward	-	0.19	0.26	0.25
	Reverse	-	0.17	0.27	0.33
5	Forward	-	0.00	0.00	-
Mean		0.30	0.21	0.25	0.22
Std Dev		0.36	0.13	0.18	0.16
Filt. Mean		0.20	0.20	0.28	0.18
Filt. Std		0.10	0.07	0.04	0.13

Figure 10 shows the adsorbed energy along the hole-to-hole path for the three nanotubes considered in this work. From these data, we can obtain the migration barriers for all paths considered. The values are presented in Table 3, together with the averaged barriers, the sizes of the three nanotubes, and the number of atoms in the unit cell. The table shows that the mean barriers obtained are compatible between all nanotube lengths, so no distinction can be made here. On the other hand, the mean difference in adsorption between equivalent positions is 0.107 ± 0.044 eV between lengths 2 and 3 and 0.072 ± 0.046 eV between 1 and 3. While the difference is larger than the standard deviation, the shift is physically negligible in the context of the adsorption values. It is of note that the forward barrier associated with leaving the vicinity of the nanotube decreases significantly with a smaller nanotube. Therefore, considering this fact, along with the small difference in adsorption, equivalent barriers, and the almost doubled size of the larger CNT (leading to larger periodicity in the system), we can expect that, overall, a shorter nanotube would be preferable to a longer one since it provides similar atomic mobility while allowing the inclusion of more Na atoms in the unit cell and

providing a smaller probability of pinning. It would be worthwhile to confirm whether these trends are maintained for larger (and different types of) nanotubes.

Adsorption for different nanotube lengths

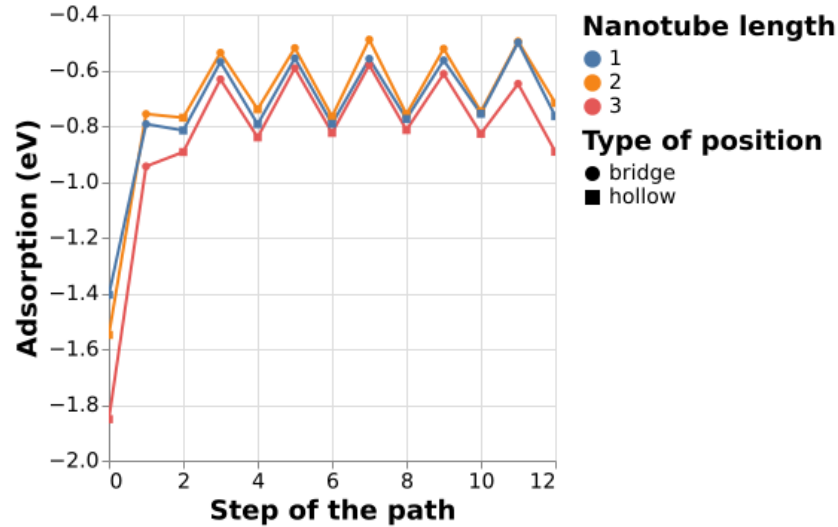


Figure 10. Adsorption energy along the hole-to-hole path for each nanotube length, only for the sodium atom.

Table 3. Migration barriers in eV for the paths in Figure 10, calculated as the difference between contiguous positions. Filt. Std displays the standard deviation with large outlier values removed. z period. represents the periodicity on the Z axis.

Step	Path Length Direction	Hole to Hole		
		1	2	3
1	Forward	0.61	0.79	0.91
	Reverse	0.02	0.01	0.00
2	Forward	0.25	0.23	0.26
	Reverse	0.22	0.20	0.21
3	Forward	0.24	0.22	0.25
	Reverse	0.24	0.25	0.23
4	Forward	0.23	0.28	0.24
	Reverse	0.22	0.27	0.23
5	Forward	0.21	0.24	0.20
	Reverse	0.19	0.23	0.21
6	Forward	0.26	0.25	0.18
	Reverse	0.26	0.22	0.24
Mean		0.25	0.27	0.26
Std Dev		0.13	0.18	0.21
Filt. Mean		0.23	0.24	0.23
Filt. Std		0.02	0.02	0.03

Finally, in order to confirm the validity of our approximation (obtaining the energy barrier via the difference between the hollow and bridge sites), we perform calculations based on the nudged elastic band (NEB) methodology between the neighboring green hollow sites of Figure 5 in the hole-to-hole area for the shorter CNT. Figure 11 presents the migration curve obtained for this calculation. The curve is obtained using 10 images with a spring constant between the images of 1.0 eV/Å². The calculation converges when three criteria have been met: a

displacement lower than $0.05 \text{ \AA}$, a force smaller than $0.05 \text{ eV/\AA}$, and an energy difference smaller than 0.005 eV . We can see in the figure that the highest energy spans a wide area and the value is close to that obtained after fixing the Na atom in the bridge position, with the energy difference being less than 0.01 eV (0.24 eV for the NEB vs. 0.23 eV from the left hollow to the bridge). Note that the Na (or Li) atoms can be slightly displaced from the original hollow site, but, due to the wide top range, the energy barrier can be correctly extracted from the energy obtained at the bridge site in the selected hollow-to-hollow movement. We expect that similar behavior could be found in the other migration processes—at least in the hole-to-hole area. For this reason, we posit that our consideration of the bridge site as the saddle point in the migration curves can lead to acceptable estimations in calculating the migration barrier.

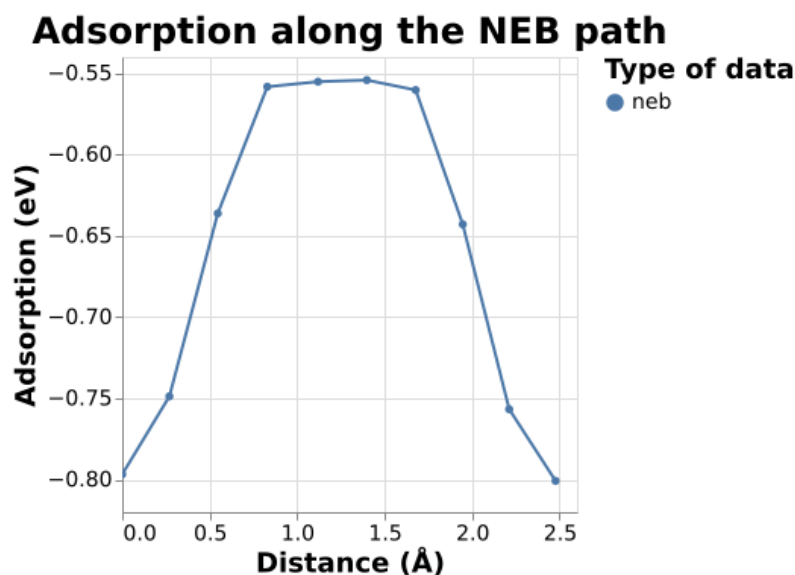


Figure 11. Adsorption energy for every NEB image against the distance between the Na position in the image and the initial position. The initial and final positions correspond to steps 2 and 3 of the hole-to-hole path for the shortest nanotube, respectively.

3.3. Charge Transfer

Finally, we analyze the charge transfer across three scenarios: (i) comparing the Na and Li atoms across all three paths in Figure 5; (ii) comparing multiple ions in the paths shown in Figure 6; and (iii) examining only Na in the hole-to-hole path for different nanotube lengths (matching the preceding adsorption analysis). Higher charge transfer corresponds to a more ionic bond, which allows for higher mobility in comparison to a covalent one, which would fix the atom in place.

Note that these data are obtained using Löwdin population analysis and the Gamma point; however, reference tests were performed using Mulliken and Natural Population with both the Gamma point and with 32 k-points. In all cases, the Na atom ceded more charge than the reference, with the largest difference (5% more) occurring with Natural Population and 32 k-points. This means that, at worst, Löwdin population analysis in the Gamma point underestimates how much charge is being transferred, making it a good reference.

3.3.1. Sodium vs. Lithium

Figure 12 displays the charge retained by the Li (a) and Na (b) in our calculations. The results show higher charge transfer for lithium than sodium overall, which is expected, but sodium still cedes roughly half its charge, reaching as high as 59% and as low as 42%. Interestingly, the hole-to-hole path has very uniform charge transfer despite having

non-negligible migration barriers, while the opposite is true for the out-tube path, which has near-null migration barriers while varying significantly in charge transfer.

Ion charge for all paths

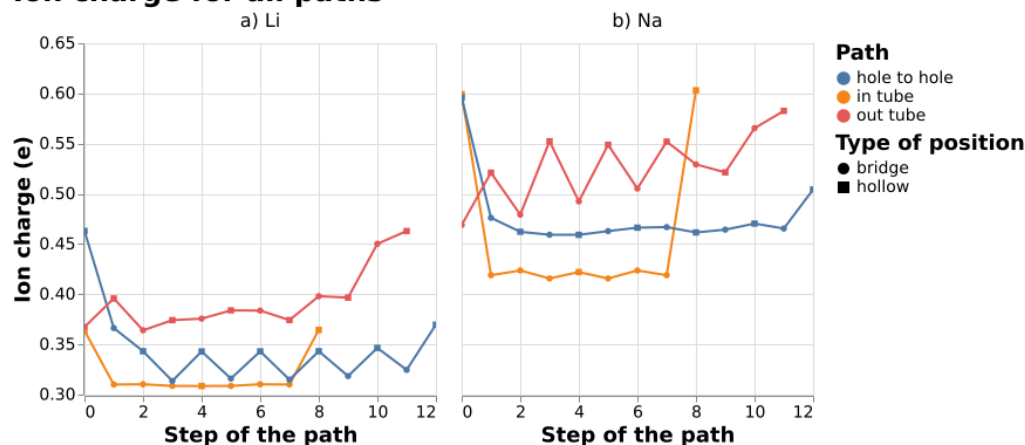


Figure 12. Charge (in electron charge (e) units) of the (a) Li and (b) Na atoms along the paths in Figure 5, which corresponds to Figure 7.

In general, charge transfer does not appear to correlate directly with adsorption or stability. This is reasonable because there are other factors that affect stability, such as the structural deformation caused by the presence of the atom or the type of bond, i.e., a more covalent bond will generally be more stable but this implies less charge donation.

When compared to reference calculations of the Na and Li charge in a hollow position in graphite (35% for Na and 20% for Li), it is clear that pillared graphene underperforms in the context of charge transfer, albeit only by a small margin in the interior of the nanotube. This is not ideal but it is expected, since, in general, the atoms have fewer carbon atoms in their vicinity at any given point when compared to graphite; moreover, when they are surrounded by carbon (the interior of the nanotube), they perform similarly to graphite.

Finally, looking at the charges of individual carbon atoms, it becomes clear that, when the atom is near the nanotube, the ceded charge tends to stay relatively localized (>80% of the charge is contained in the nearest 50 atoms), whereas, in the more graphene-like regions, it tends to diffuse to a greater extent throughout the structure.

3.3.2. Multiple Atoms

It is important to note that FIREBALL simulates an infinite lattice; therefore, the system is not connected to any external contacts through which the transferred charge can be drained, meaning that, as more atoms are added, the total charge increases. This would not be the case in a real system, which would likely increase charge transfer.

Figure 13 shows that, for the closest positions (in the case of Na), the atoms retain a significant amount of charge; however, as soon as they move on to the next hollow (corresponding to a density of one Na atom per six C atoms), they retain significantly less charge. In fact, the hole-to-hole path stabilizes at a value similar to the single-atom cases—practically at step 2. The higher value of the hole-to-hole path compared to the single-atom case is due to the fact that the figure shows the mean charge of all extra ions, and the static atom is permanently placed at the 0th position of the hole-to-hole path, which has the highest charge retention in the single-atom case. The other two paths show a similar trend of higher retention when the atoms are closer but do not stabilize as quickly. This is likely also due to the fact that these paths have no sites near the nanotube, meaning that charge retention decreases for both atoms and not only one as in the hole-to-hole case. It is also interesting that the 0th step of the top-bottom path retains significantly less charge

than the other two, although this is readily explained by the extra distance added by the graphene layer between the atoms. Furthermore, it is clear that Li retains similar charge throughout, regardless of separation.

The three-atom case shown in Figure 14 shows a very similar behavior to the two-atom case, with much more charge retention in the closest step, and a rapid decrease to a value similar to the single-atom case as the atoms get farther apart.

Ion charge for all paths

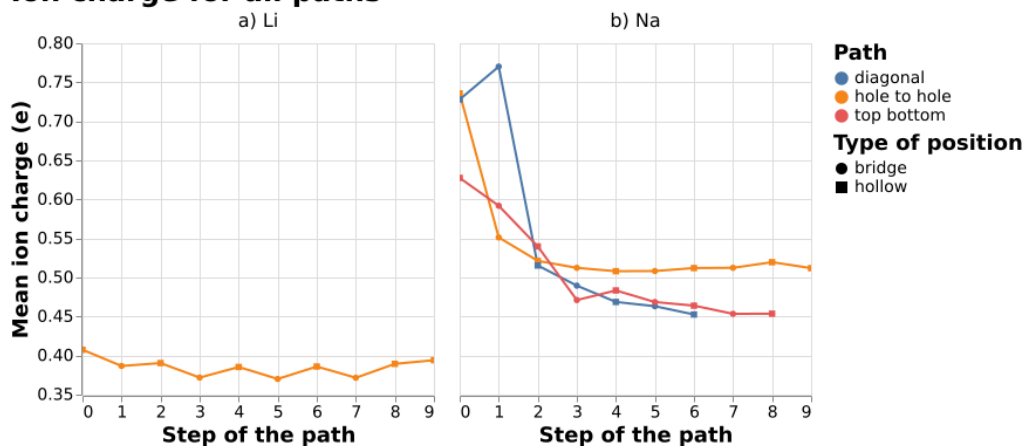


Figure 13. Mean ion charge along paths (a–c) of Figure 6 for Na and only path (a) for Li (b) for Na.

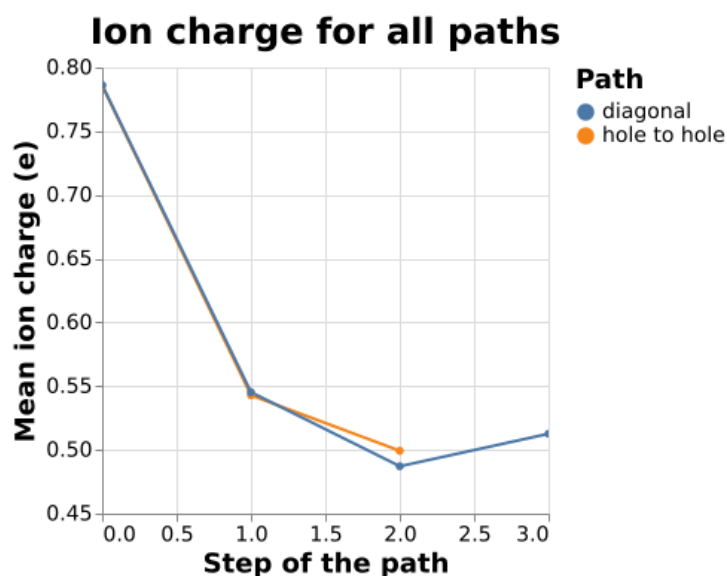


Figure 14. Mean ion charge along paths (d,e) of Figure 6 for Na. All positions are hollow sites.

3.3.3. Nanotube Length

Figure 15 shows no clear correlation between the nanotube length and charge transfer for the sodium atom. This result is consistent with the previous adsorption analysis and is favorable in terms of greater freedom when designing an anode using this structure, since the nanotube length would not condition the transfer capabilities.

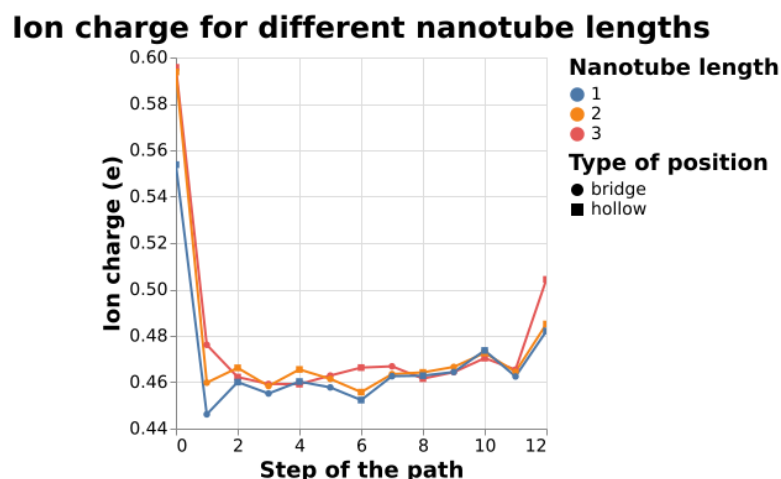


Figure 15. Charge of the sodium atom along the hole-to-hole path for different nanotube lengths.

4. Discussion

Our main goal is to provide—by means of theoretical simulations based on DFT—a proof of concept for the use of pillared graphene as an electrode in future Na-ion-based batteries by comparing the behavior of Na with that of Li. Specifically, we have focused our attention on the structural stability, Na/Li transport kinetics, and electronic properties of pillared graphene. By systematically altering structural parameters such as alignment, the nanotube length, and mechanical separation, we demonstrate how these structures could, in principle, address the limitations of traditional graphite anodes regarding sodium storage, achieving comparable performance to lithium in all cases.

The first result concerns the pillared structure itself. We have found a preference for a staggered configuration of the pillars, which stems from the formation of stable heptagonal junctions at the CNT–graphene interfaces. This bond formation was previously proposed by Yang et al. [50], but, in their study, the authors performed the calculations with a single graphene layer. Repeating the graphene–CNT structure in the Z-direction aligns the CNTs of consecutive cells, which complicates bond formation at the CNT–graphene interface. On the other hand, the staggered CNT maintains junction stability throughout the structure. The small energy change as the structure is stretched also indicates good resistance to mechanical stress, which agrees with previous works. Interestingly, the structure remains similar and the stability is slightly increased when the CNT size is reduced. The intercalation of the CNT also increases the spacing, favoring the adsorption and mobility of the Na atoms, as has been shown. Furthermore, the flexibility of pillared graphene is a positive factor for battery anodes, which must tolerate repetitive strain during charge–discharge cycles without structural degradation.

After identifying the most stable configuration of pillared graphene, we proceeded to include one Na or Li atom at different positions to analyze three important parameters: the adsorption energy, migration barriers, and charge transfer. Given that lithium is used in current batteries, similar performance for Na and Li in these three parameters could indicate that pillared graphene is a good choice for a future electrode. Generally, we found that all positions studied presented a negative adsorption energy, suggesting the good accommodation of Na and Li in the structure. Sodium generally shows higher adsorption than lithium, with the positions in and close to the CNT being the most favorable. More importantly, the data obtained show better values than in the standard graphite case. This can be considered a relevant improvement, especially for Na, given that it is unstable in graphite, as reported previously [11]. When more atoms are added, adsorption does indeed decrease compared to the single-atom case. The effect is more pronounced as the atoms

grow closer together; when they are separated by at least one hollow site, they exhibit similar adsorption to the single-atom case. Interestingly, when the atoms are closest, the effect is more pronounced for Na, and, when they are farther apart, it is more pronounced for Li.

Pillared graphene also demonstrates adequate atom mobility. Although sodium intercalation in bulk graphite is traditionally hindered by unfavorable thermodynamics, ARM-60 provides viable migration barriers for sodium, remaining below 0.31 eV for all paths and nanotube lengths and generally lying around 0.23 eV in the graphene-like region and 0.22 eV in the interior of the nanotube, with much lower values outside the nanotube (0.07 eV). This represents a significant improvement over bulk graphite, with an interlayer distance of 3.4 Å (1.77 eV), and it is also lower than observed in other bulk graphite calculations at higher interlayer distances of 4.5 Å (~0.3 eV [12,52]). However, it is slightly higher than the value obtained in our own calculations of bulk graphite at 4.5 Å (0.19 eV). This could be due to multiple factors. One explanation is that the curvature of the graphene sheet can increase the migration barriers [54,55]; however, this is not entirely a negative aspect, since, due to the high elasticity of pillared graphene, it is possible that the curvature could be mitigated mechanically. Another explanation is that our reference calculation was performed with a 4.5 Å graphene–graphene distance to facilitate comparison with previous theoretical works. Calculating this separation from scratch in FIREBALL could yield a slightly different baseline, which would also modify the migration barriers. Regardless, the difference between the graphite calculation and pillared graphene is within a standard deviation, and the values are comparable to those of previous theoretical works. Furthermore, the barriers remain comparable between Na and Li across all cases, with Li exhibiting slightly lower barriers in the graphene-like area and Na outperforming on the exterior of the nanotube; this would, in theory, allow diffusion in all directions. The migration barriers obtained with two atoms remained indistinguishable from those given by a single atom when the separation between the two increased beyond one hollow site. However, when the atoms were close, the barriers were noticeably lower in the forward direction and higher in the reverse. We must stress that all energies obtained in this work should be validated with further plane-wave codes using better exchange and correlation functionals and including vdW interactions.

The high energy barriers predicted near the CNT–graphene junctions may limit the electrochemical performance of pillared graphene by reducing Na mobility. Similar limitations may also arise in other expanded graphene architectures where the graphene sheets are separated by organic molecules. Depending on their chemical nature, these molecules may either attract or repel Na ions, thereby affecting both ion storage and transport. Alternative approaches to enhancing Na adsorption include defect engineering through ball milling or mild oxidation, as well as heteroatom doping. However, stronger adsorption does not necessarily translate into improved performance, since excessively favorable adsorption sites may act as pinning centers that hinder ion diffusion. Therefore, irrespective of whether the modification is structural or chemical, the key challenge is to achieve an optimal balance between enhanced adsorption and sufficiently low diffusion barriers, avoiding excessively strong binding that could compromise long-range Na or Li transport. Interestingly, N doping has been reported to enhance Na adsorption while maintaining relatively low migration barriers, suggesting that improved adsorption and fast ion diffusion are not mutually exclusive [53]. Future work should systematically compare these different strategies using a consistent computational methodology. In particular, combinations of pillared architectures with N doping, defect engineering, or tailored molecular spacers could provide a promising route toward materials that simultaneously promote Na adsorption

and high ion mobility. Our multi-atom analysis also indicates that more atoms will help with mobility near these pinning sites through inter-ionic repulsion.

The last parameter under consideration is charge transfer. This quantity reflects the ease with which the atom donates its charge to the environment, which is fundamental to the operation of an ion-based battery. Our analysis of charge transfer confirmed that sodium retains only 42–59% of its valence charge, independently of the nanotube length. This means that it retains more charge than Li in the same structure, but it is close enough to consider the Na atom as an adequate alternative. Although slightly higher than in traditional graphite, where we found retention of 35%, the nature of the proposed structure remains ionic in all sites studied. It is important to note that these results were obtained in an isolated structure, not connected to an external circuit, which would certainly affect charge transfer. Furthermore, the charge tends to be slightly more localized near the nanotubes, whereas it diffuses more homogeneously throughout the structure when farther away from them. The multi-atom analysis also indicates that excessively high concentrations increase retention, although separation of one hollow provides similar retention to the isolated atom. When the atoms are placed above and below the graphene sheet, they also transfer charge more easily due to the increased distance provided by the sheet. This means that it may be possible to obtain a saturated structure with atoms both above and below each graphene layer, mitigating the impact of the large interlayer distance on the energetic density.

Overall, our theoretical DFT findings suggest that pillared graphene is a promising material, not only for H₂ storage but also as a battery electrode. The nanotubes provide ample interstitial space to accommodate Na atoms. Although excessive empty volume can lower the energy density, the expanded interlayer distance opens up the possibility for more than one atom to be located at a given XY position since they have space to separate in the Z axis, potentially offsetting these losses and enhancing the energy density. While these computational results serve primarily as a proof of concept, they provide strong rationale for further investigation. Future computational studies could implement more accurate exchange-correlation functionals or, conversely, utilize lower-cost methods to simulate larger-scale structures with hundreds of Na atoms. Such scaling would allow the preliminary evaluation of macroscopic metrics like the theoretical capacity and open circuit voltage, alongside thermodynamic effects such as temperature. Additional theoretical avenues include assessing Na clustering and metallic plating. Ultimately, the experimental synthesis and prototyping of pillared graphene electrodes, building upon earlier experimental frameworks [36], will be necessary to validate these predictions.

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Nomenclature

Acronyms and Abbreviation

ARM-60	A structural model consisting of a 10×10 armchair graphene sheet joined to a (6, 0) zig-zag carbon nanotube
CNT	Carbon nanotube
DFT	Density Functional Theory
LDA	Local density approximation
McWEDA	Multi-center weighted exchange-correlation density approximation
NEB	Nudged elastic band
vdW	van der Waals (interactions/forces)

Symbols and Variables

E_{ads}	Adsorption energy of an atom on the pillared graphene structure
E_{TOT}	Total calculated energy of the combined system (pillared graphene + intercalated atom)
E_{PGR}	Energy of the isolated pillared graphene structure
$E_{Na(Li)}$	Energy of the isolated Na (or Li) atom, calculated in its corresponding bulk structure
r_s, r_p	Cutoff radii for the s and p atomic orbital wavefunctions, respectively
Γ point	Gamma point; the center of the first Brillouin zone in reciprocal space used for k -point sampling
Z-axis	Axis perpendicular to the graphene sheets, denoting the direction of the interlayer spacing and nanotube alignment

Defined Structural Terms

Hollow site	An adsorption position located at the center of a carbon hexagon
Bridge site	An adsorption position located directly above the bond between two adjacent carbon atoms
Out-tube	Migration path along the exterior surface of the carbon nanotube
In-tube	Migration path along the interior of the carbon nanotube
Hole-to-hole	Migration path across the flat, graphene-like region between two carbon nanotubes

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