sp–sp2 Carbon Sheets as Promising Anode Materials for Na-Ion Batteries

Seunghan Lee, Jahyun Koo,* Minwoo Park, and Hoonkyung Lee*†

Department of Physics, Konkuk University, Seoul 05029, Korea

ABSTRACT: We explore the applicability of graphynes, two-dimensional carbon sheets with sp- and sp2-bonds, as sodium (Na)-ion battery anodes using first-principles density functional theory. We found that voltages attainable from the charging–discharging of Na into multilayer graphyne are proper for use as anodes. The composite is C3N4 at the maximum Na concentration, corresponding to gravimetric and volumetric capacities of ~837 mAh g−1 and ~1056 mAh cm−3, respectively. These are significantly greater than the corresponding values (372 mAh g−1 and 818 mAh cm−3) of graphite for lithium. We ascribe the enhancement of the capacities to their nanoporous structures with sp- and sp2-bonded carbon atoms, which effectively bind multiple Na atoms. We propose that sp–sp2 carbon sheets can be promising candidates for high-capacity Na-ion battery anodes.

1. INTRODUCTION

The lithium-ion battery (LIB) is one of the widely used batteries for portable electronics because of its high energy density and safe source of power. Graphite has been widely employed as an LIB anode material because the device with graphite anode has demonstrated high power density with a high stability for lithium intercalation (small volume change), and a gravimetric capacity that is as large as 372 mAh g−1.1−4 However, lithium is an expensive element, increasing the overall cost of the materials for the commercialization of LIBs.5 In contrast, sodium is a low-cost element because of its abundance6 (Na: 0.09−0.46 $/kg, Li: 5.09−5.56 $/kg) and is the second lightest element among the alkali metal elements.

Recently, sodium (Na)-ion batteries (SIBs) have been considered as cost-effective batteries replacing LIBs. However, unlike LIBs, the relevant negative electrodes (anodes) are yet to be found, and graphite cannot be used as an insertion host material of Na ions. This could be generated from the difference between Na and Li: the ionic radius (0.97 Å) of Na is much larger than that of Li (0.68 Å) and the ionization potential of Na is lower than that of Li by 0.25 eV, inhibiting Na interaction with graphite, unlike Li.7,8 Recent studies have been performed on the possible candidates for the anodes of SIBs, such as hard carbons (nongraphitizable carbon), some oxides, p-block elements, sulfides, and tin.9–12 However, these materials have several issues such as their poor reversibility.

We explored the possibility of using multilayer graphynes (graphyne is an sp–sp2 hybrid carbon atomic layer consisting of sp2-carbon atoms and acetylene groups (−C≡C−)), which are layered-structured materials. γ-Graphyne is semiconducting with a band gap of 0.47 eV13 and has the lowest energy among sp–sp2 carbon sheets and a higher energy than graphene or graphite by 0.63 eV atom−1.14 Detailed information on the geometrical and electronic structures of extensive sp–sp2 carbon sheets is provided in the literature.15 For the anodes of SIBs, we consider two-dimensional layers of sp- and sp2-bonded carbon atoms. This is because they are expected to have a small volume change due to their layered structures and are high-power anodes due to the high mobility of the Na atom between layers. In addition, the feasibility of multilayered graphyne and graphdiyne for high-capacity and high-mobility anodes of LIBs has already been demonstrated.16−23 Certain criteria are required of candidates for anodes of SIBs. (1) The average voltage by sodiation/desodiation should range from ~0 to 1.5 V when a Na metal bulk is used as an electrode connected to Na-intercalated systems. (2) In addition, the gravimetric and volumetric capacities should be as high as those of graphite for the anode of LIBs, which are 372 mAh g−1 and 818 mAh cm−3, respectively. Here, we searched for new anodes of SIBs based on multilayer sp–sp2 carbon sheets, graphyne, meeting the criteria for the anodes of SIBs. On the other hand, progress has been made in the synthesis of these anodes: sp–sp2 carbon sheets such as graphynes were synthesized using a bottom-up method24 and graphdiyne, which is made up of sp2-carbon atoms and diacetylene groups (−C≡C−C≡C−), was made in the form of powders and flakes.25−27 Carbon enyne, a carbon layer structure consisting of diacetylene groups and sp2 carbon atoms, was also successfully synthesized in a film form.28 More recently, an ultrathin graphdiyne film on graphene was synthesized using solution-phase van der Waals epitaxy method.29 These results suggest that new carbon allotropes of sp–sp2 carbon sheets could be synthesized.
2. COMPUTATIONAL DETAILS

Our calculations using the density functional theory\textsuperscript{30} were carried out with the Vienna ab initio simulation package using a projector-augmented-wave method.\textsuperscript{31} The generalized gradient approximation in the Perdew–Burke–Ernzerhof scheme\textsuperscript{32} was employed and the kinetic energy cutoff was set at 400 eV. We employed a $2 \times 2$ hexagonal supercell graphyne system containing 48 carbon atoms. During geometrical optimization of Na-dispersed graphynes, its equilibrium lattice constant was fixed equal to the isolated $2 \times 2$ graphyne. The geometrical optimization was performed until the Hellmann–Feynman force acting on each atom was less than 0.01 eV Å$^{-1}$. The first Brillouin zone integration was performed adopting the Monkhorst–Pack scheme.\textsuperscript{33} A $4 \times 4 \times 1$ k-point sampling was performed for the $2 \times 2$ graphynes. To remove spurious interactions between periodic images because of periodic calculations by the long-range Coulomb interaction, the vacuum layer in each of the nonperiodic directions was $\sim 10$ Å.

3. RESULTS AND DISCUSSION

To explore the SIB anodes, we considered γ-graphyne for the Na adsorption material, in which there are hexagonal and triangular geometries made up of sp- and sp$^2$-bonded carbons. γ-Graphyne was found to be the most stable among the sp–sp$^2$ carbon atomic layers.\textsuperscript{34–37} Hereafter, we use “graphyne” to refer to “γ-graphyne”. We performed calculations on the Na atom attached to a single-layer graphyne to determine the optimal adsorption location and to investigate the adsorption principle. We found that Na adsorption depends only on the local geometries such as hexagon and triangle sites. Figure 1a,b show the atomic structures of the Na-dispersed graphynes with a $2 \times 2$ supercell when a Na atom is bound to a hexagon and triangle site, respectively. For convenience in comparison with the existing graphitic anode materials, the C$_{48}$Na$_x$ is reduced to C$_2$Na$_x$. The binding energy of Na atoms is defined by $E_{\text{bind}}(\text{Na}) = (E_c + N \cdot E_{\text{Na}} - E_{\text{C}_{2}\text{Na}_{x}})/N$, where $N$ is the number of Na atoms attached per $2 \times 2$ supercell for a given $x$, $E_{\text{C}_{2}\text{Na}_{x}}$ is the total energy of Na dispersed in a $2 \times 2$ graphyne with $x$ concentration of Na atoms, $E_c$ is the total energy of a $2 \times 2$ isolated graphyne, and $E_{\text{Na}}$ is the total energy of an isolated Na atom in vacuum. The Na binding energies for the triangle and hexagon sites were calculated to be 2.46 and 1.78 eV, respectively, which indicates that Na energy prefers to bind to a triangle site than to a hexagon site.

To investigate the binding mechanism of Na, the charge density difference was calculated (Figure 1c–f). The charges are transferred from the Na atom to the graphyne. The in-plane projected charge densities as a function of $z$ are shown in Figure 1g,h, which are almost the same in both cases. Our Bader charge analysis\textsuperscript{38} shows that 0.88 and 0.78 electrons per Na move to the triangle and hexagon of graphyne, respectively. An attractive feature is that the Na binding energy on the triangle is larger than that on the hexagon because the sp$^2$-bonded carbon atoms are more reactive than the sp$^2$-bonded carbon atoms. Unlike graphitic materials, the sp$^2$-bonded carbon atoms in graphyne present attractive binding conditions for Na.

The Na atoms are placed over the graphyne sheet by $\sim 2$ Å. On the graphyne sheet, a Na atom adsorbs on a center of the triangular site with a binding energy of 2.46 eV/Na (see Figure 1b). The shortest Na–C distance is 2.68 Å and the Na atom is located at a height of 1.7 Å above the graphyne sheet. Because Na atoms have a large ionic radius, the binding length of Na atoms is farther than when lithium is adsorbed. The composites of the Na-dispersed graphynes shown in Figure 1 are C$_2$N$_{4x}$. The Na binding energy on a graphyne sheet (2.46 eV) is greater than the cohesive energy of bulk Na (1.10 eV). We, therefore, expect that the Na atoms can be dispersed on graphynes without segregation of the Na atoms.

We studied the optimized geometries of Na-dispersed graphynes as the concentration of Na varies (Figure 2a–d). We considered the case where only one side of the sodium is adsorbed to figure out the tendency of Na adsorption on graphyne because our final goal was to investigate the possibility of multilayer graphyne as an SIB. From the case of one Na atom attached, we found that the most favorable adsorption site of Na is the triangles. When the Na concentration was low, at $x = 0.250$ (Figure 2a), the triangle site was only partially filled by Na atoms. Near the concentration of $x = 0.875$ (Figure 2b), the hexagon site starts to be filled. When the concentration was $x = 1.500$ (Figure 2c), all of the triangle and hexagon sites were filled with one Na atom. Na atoms migrate from the hexagon site to the triangle site as Na atoms are consecutively added. Unlike lithium adsorption on graphyne, where the maximum concentration of Li is C$_2$Li$_{144}$ the maximum concentration for Na adsorption is C$_2$Na$_{2x}$, where all triangle sites are filled with 2 Na atoms (Figure 2d). Figure 2e shows the calculated binding energy of Na atoms on single-layered $2 \times 2$ graphyne
Figure 2. Atomic structures of Na-dispersed single-layered graphyne with different concentrations of Na: (a) \( x = 0.250 \), (b) \( x = 0.875 \), (c) \( x = 1.500 \), and (d) \( x = 2.000 \) from C\(_6\)Na\(_x\). (e) Calculated binding energy as a function of the concentration of Na atoms.

as a function of the Na concentration \( x \). According to the binding energy, single-layer graphyne has the potential for attaching more Na atoms than its concentration \( x > 2 \). However, we cut our maximum concentration as \( x = 2 \) for single-layer graphyne. Because the Na concentration is larger than 2, the Na atoms form a second layer structure, which can cause large volume expansion. It is an inconsistent structure for application of multilayer graphyne battery anode, which is our ultimate goal.

To use realistic anode materials, now we carried out calculations on Na intercalation to multilayer graphyne. Figure 3a shows the schematic illustration of SIBs with the multilayer graphyne as an electrode. We then investigated the stability of Na dispersion on multilayer graphynes. We only consider the cases where the Na binding energy of multilayer graphyne is larger than (or very close to) the cohesive energy of bulk Na. This indicates that Na-dispersed graphynes for a given \( x \) is energetically more stable than the segregated phase between bulk Na and graphynes. For the propose of calculation, the open circuit voltage \( V_{oc} \) is defined as a function of \( x \)

\[
V_{oc}(x) = \frac{(E_{C} + NE_{Na}^{bulk} - E_{C-Na}^{x})}{eN}
\]

(1)

where \( e \) is the elementary charge and \( E_{Na}^{bulk} \) is the total energy per Na in a body-centered cubic Na (eq 1), which meets the criterion for the voltage for the SIB anodes. The negative values of the voltage mean that the segregation between bulk Na and graphynes is energy favorable.

Based on the Na binding structure of single-layer graphyne, we first considered AA-stacked multilayer graphyne. Unlike graphite, which is endothermic for Na intercalation, we found that AA-stacked multilayer graphyne is exothermic for Na intercalation, where the interlayer distance is 3.1 Å. The tendency of sodium adsorption geometry retained in the result of sodium intercalation of single-layer graphyne. On AA-stacked multilayer graphyne, the triangle sites are filled with one or two Na atoms as the concentration of Na increases up to approximately \( x = 1.625 \). At the higher concentration of \( x = 1.625 \), the hexagon sites begin to be filled with Na atoms. However, at the maximum concentrations, namely, \( x = 2.25 \), all triangle sites are filled with two Na atoms (Figure 3b,c), corresponding to the gravimetric and volumetric capacities of C\(_6\)Na\(_{2.25}\) of 837 mAh g\(^{-1}\) and 1056 mAh cm\(^{-3}\), respectively, much larger than those of graphite for lithium (372 mAh g\(^{-1}\) and 818 mAh cm\(^{-3}\)). The tendency of the occupation of Na atoms is consistent with that on single-layer graphyne. The layer–layer distance is increased up to 4.1 Å by Na intercalation and up to three Na atoms are intercalated at a triangle site with different heights with respect to the graphyne plane. In contrast, the maximum concentration of Na on monolayer graphyne is C\(_6\)Na\(_{1.5}\) which is lower than that of multilayer graphyne. These results show that the Na capacity of multilayer graphyne could be higher than that of a monolayer one. We found that the interlayer distance in Na-intercalated graphynes has a weak dependence on the concentration \( x \). The voltage by Na intercalation on multilayer graphynes slightly increases compared with that on single-layer graphynes. The voltage by Na insertion was calculated as the Na concentration increases (Figure 3d). Importantly, the voltage and capacity of AA-stacked multilayer graphyne meet the criteria for the anode. The magnitude of the voltage of AA-stacked multilayer graphyne becomes twice as high as that in single-layer graphyne because a Na atom interacts with both sides of graphyne, whereas the Na atom interacts with one side of single-layer graphyne.

We also considered AB-stacked multilayer graphyne for Na intercalation. Like AA-stacked multilayer graphyne, triangle sites begin to be filled with Na atoms and then hexagon sites are filled with Na atoms at higher concentrations of Na (Figure 4a–f). At the maximum concentration, \( x = 1.875 \), one or two...
Na atoms occupy triangle sites and the interlayer distance is increased. The tendency of Na intercalation is similar to that in AA-stacked graphyne. The calculated maximum gravimetric and volumetric capacities of AB-stacked graphyne reach 697.5 mAh g\(^{-1}\) and 920 mAh cm\(^{-3}\), respectively, larger than those of graphite for lithium. Since the calculated voltage and capacity of AA- and AB-stacked graphynes (Figure 4g) meet the requirements for the anode, multilayer graphyne can be used for the SIB anodes. Moreover, the AA-stacked graphyne is metallic and the AB-stacked graphyne is semiconductor with a small gap of 0.19 eV\(_{st}\), which is also an advantage when using anode materials.

In addition to the insertion capacity, the kinetics of Na ions in graphyne multilayer structures is one of the key factors for the anode. As anode materials, van der Waals stacked multilayer graphynes may have a larger Na capacity than graphite, which is made up of only sp\(^2\)-bonded carbon atoms. Therefore, we believe that sp\(^2\)–sp\(^3\) hybrid carbon sheets such as graphdiyne can also be used for the SIB anodes.

We discussed the noticeable properties of multilayer graphynes as a promising SIB anode material. The bond of Na atoms energetically prefers the sp\(^2\)-bonded carbon atom of graphyne to the sp\(^3\)-bonded carbon atom. This is ascribed to the fact that the sp\(^2\)-bonded carbon atoms are more reactive to Na than the sp\(^3\)-bonded carbon atoms. These graphyne-based SIBs have a high Na gravimetric density. For this reason, multilayer graphynes may have a larger Na capacity than graphite, which is made up of only sp\(^2\)-bonded carbon atoms. Therefore, we believe that sp\(^2\)–sp\(^3\) hybrid carbon sheets can be utilized as promising candidates for Na-ion battery anodes.

4. CONCLUSIONS

We investigated the applicability of multilayer graphynes for Na-ion battery (SIB) anodes using first-principles density-functional theory. Our investigation highlights that multilayer graphynes are promising high-capacity SIB anode materials. (1) The calculated voltages by Na intercalation were found to be suitable for the anodes. (2) The gravimetric and volumetric Na capacity of multilayer graphynes can reach ~837 mAh g\(^{-1}\) and ~1056 mAh cm\(^{-3}\), much larger than those of graphite anode for lithium-ion batteries (372 mAh g\(^{-1}\) and ~800 mAh cm\(^{-3}\), respectively). (3) Moreover, because of their layered structure with high porosity, Na would be highly diffusive in the in-plane as well as the out-of-plane directions in multilayer graphyne, leading to a high-power battery. These findings are generated from the geometric feature of multilayer graphynes because of their sp–sp\(^3\) hybrid carbon sheets and layered structures. Therefore, we propose that multilayer sp–sp\(^3\) carbon sheets can be utilized as promising candidates for Na-ion battery anodes.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: hkiee3@konkuk.ac.kr.*

**ORCID**

Jahyun Koo: 0000-0003-0128-5303

Hoonyoung Lee: 0000-0002-6417-1648

**Notes**

The authors declare no competing financial interest.

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