

DFT Investigation of the Swelling Effect in Intercalated C₃N

G.T. KASPRZAK*

Institute of Physics, Czestochowa University of Technology,
Ave. Armii Krajowej 19, 42-200 Czestochowa, Poland

Doi: [10.12693/APhysPolA.142.172](https://doi.org/10.12693/APhysPolA.142.172)*e-mail: grzegorz.kasprzak@pcz.pl

Faced with the growing demand for reliable, cheap, and easy-to-recycle batteries, scientists are faced with the task of finding new and promising electrode materials. Based on the *ab-initio* analysis of 2D carbon and nitrogen material, we found that the C₃N compound is one of the many potential candidates for use as anode material in Li- and Na-ion batteries. Here, bilayer C₃N material was studied after the intercalation of Li and Na atoms. In our previous research about monolayer C₃N, we performed first-principles calculations to investigate the geometric structure, binding energies, and band structure variations after surface ion adsorption. We found that the Li and Na atoms prefer to stay in the hollow site among hexagonal carbon rings. To find how the bilayer system degenerate, we relax the structure of the pure bilayer and with the Na and Li atoms, to discover how the Li/Na behave and how it will affect the distance between layers.

topics: C₃N, electronic properties, electrode materials, DFT calculations

1. Introduction

The world’s growing dependence on electricity, in particular on portable energy sources, poses great challenges for material engineers. The search for new materials constituting a good building block for battery electrodes is currently one of the fastest-growing branches of science. The achievements of quantum mechanics, along with the mathematical apparatus used in *ab initio* calculations developed over decades, allow for the modeling of new structures and the study of their properties. Perhaps the future of batteries is their miniaturization. For this reason, two-dimensional (2D) materials are believed to be promising materials for next-generation high-performance batteries due to their extraordinary electronic and structural properties. Very recently, attention has turned to 2D monoatomic structures, such as graphene [1], phosphorene [2–4], borophene [5], silicene [6], stanene [7], arsenene [8], and many others. Modeling materials on the atomic scale offers extraordinary opportunities to discover and test their stability. After all, graphite is made of multilayer graphene domains.

Recently, a 2D system consisting of carbon and nitrogen atoms (C₃N) was successfully synthesized by Yang et al. [9]. This novel material, with a graphene-like planar structure, resulting from a preference for *sp*² hybridization, has aroused much attention. C₃N has been shown to exhibit excellent mechanical, thermodynamic, and electrical properties that are beneficial for its application in various fields [10, 11].

This paper is a continuation of the study of the C₃N monolayer through the first-principles DFT calculations. We found that the Li and Na atoms prefer to stay in the hollow site among hexagonal carbon rings, and the second most favorable site is the bridge site on the bond of C–C. The maximum theoretical storage capacity for partial-layer adsorption of C₃N only is calculated to be 267.81 mA h/g [12].

2. Computational methods

To study the electronic properties of investigated material, first-principles calculations are performed within the framework of the density-functional theory (DFT) [13] implemented in the Quantum Espresso package [14]. The generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) is used for the exchange-correlation functional together with the projector-augmented wave (PAW) method. A vacuum of 20 Å along the *z*-axis was applied to prevent interlayer interactions from the periodic images. Van der Waals forces were taken into account in the simulation.

3. Results and discussion

The crystal structure of the C₃N monolayer has a *P6/mmm* symmetry with a hexagonal lattice. As in the case of graphene, C₃N has a flat structure since all C and N atoms are *sp*² hybridized. The results of the Quantum Espresso relaxation of two

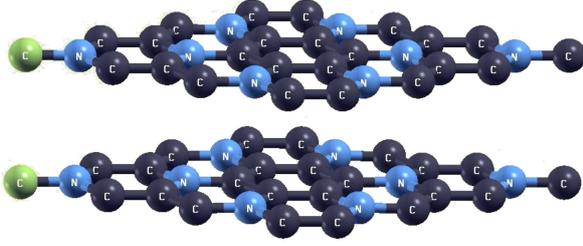


Fig. 1. Distance (3.3376 Å) between layers and surfaces of C_3N .

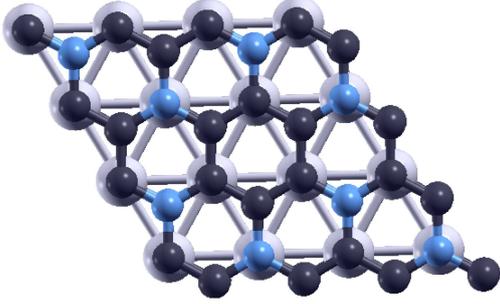


Fig. 2. Starting positions with intercalated Li/Na atoms between C_3N layers (top sites).

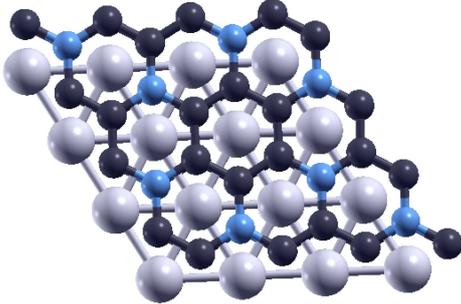


Fig. 3. Starting positions with intercalated Li/Na atoms between C_3N layers (hollow sites).

layers with 32 atoms in the layer, and a total of 64 atoms in the cell gave us a distance between layers of 3.33 Å, as shown in Fig. 1. The measured distance is between atoms represented by the green color. The binding energy between two layers was calculated with a formula

$$E_b = 2E_{C_3N_{\text{monolayer}}} - E_{C_3N_{\text{bilayer}}}, \quad (1)$$

where $E_{C_3N_{\text{monolayer}}}$ and $E_{C_3N_{\text{bilayer}}}$ denote the total energy of one layer and two layers, respectively. Total energies and binding energy are included in Table I. The negative value of the binding energy suggests that the presented bilayer system is energetically more favourable at temperature of 0 K. To study the degeneration after the intercalation process, we used 16 atoms Li/Na and put them between the layers in the two starting positions, i.e., top sites (Fig. 2) and hollow sites (Fig. 3).

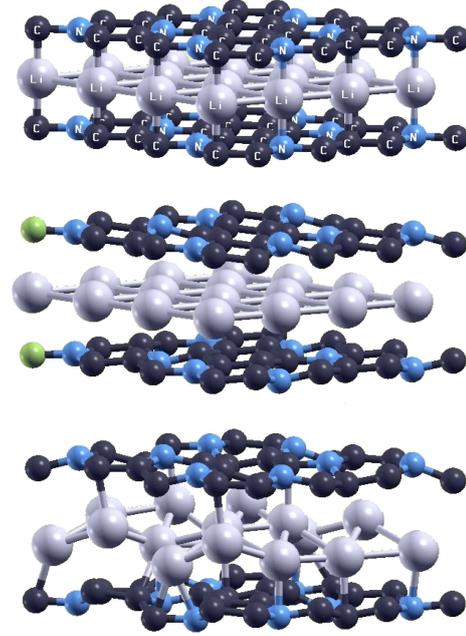


Fig. 4. Degenerating structure with intercalated Li atoms between C_3N layers (top sites).

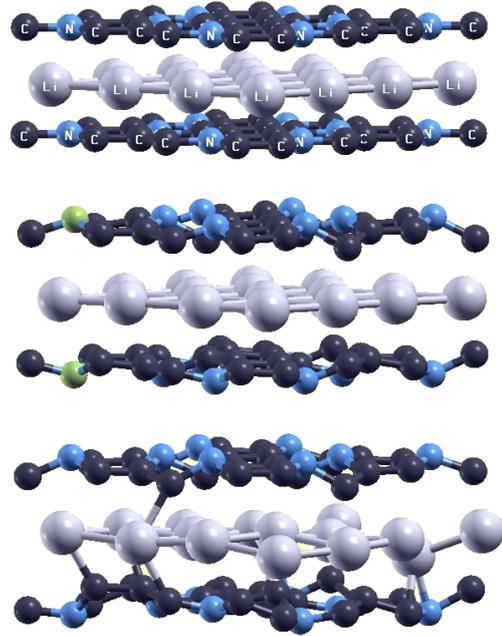


Fig. 5. Degenerating structure with intercalated Li atoms between C_3N layers (hollow sites).

In both cases, the distance between the layers significantly increases and the structure degenerates, as it is shown in Figs. 4 and 5.

Further calculation after Li/Na intercalation shows how this material degenerates. As a starting position, we used a relaxed structure with a starting 3.33 Å distance between layers. The starting positions with Li/Na atoms are shown in Figs. 2

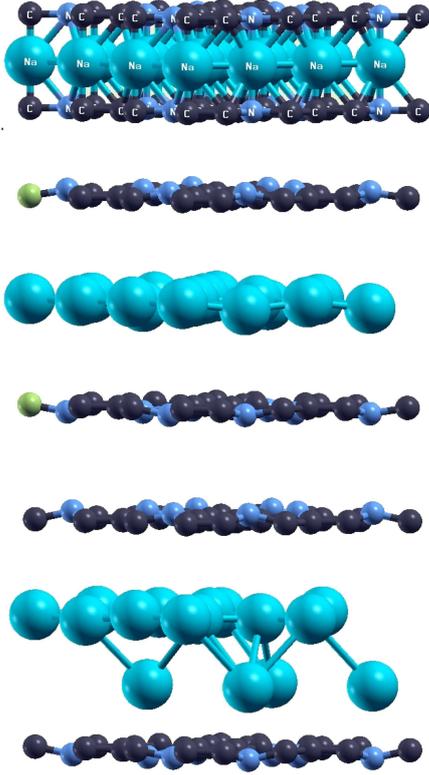


Fig. 6. Degenerating structure with intercalated Na atoms between C_3N layers (top sites).

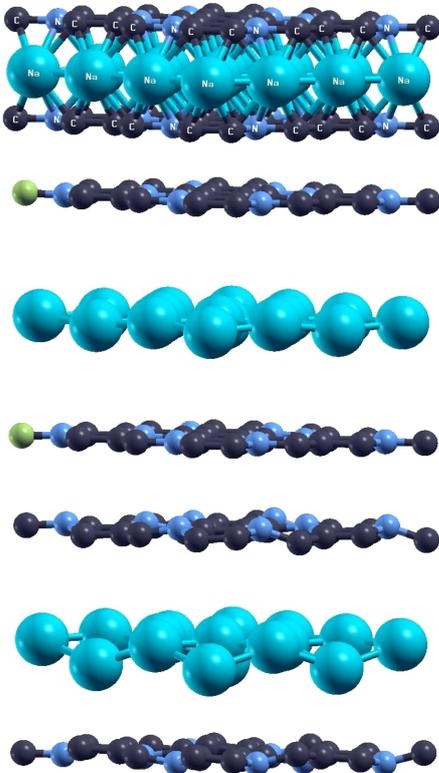


Fig. 7. Degenerating structure with intercalated Na atoms between C_3N layers (hollow sites).

TABLE I

Calculated total energies (E_{tot}) and binding energy between two layers (E_b) for C_3N .

	$C_3N_{\text{monolayer}}$	C_3N_{bilayer}
E_{tot} [Ry]	-648.0843	-1295.2294
E_b [Ry]	-0.9391	

and 3. The degenerates of this material after Li intercalated are shown in Fig. 4 (top sites) and Fig. 5 (hollow sites). After changing the Li to Na atoms, the degeneration of the structure is shown in Figs. 6 and 7. The calculation shows that the intercalated 16 atoms between the layers of 32 atoms in a layer mostly degenerate it. In the case of Na intercalated atoms, the distance between the layers is higher than the Li intercalation. In both cases, the distance between the layers increases significantly, which corresponds with the swelling effect observed in real materials.

4. Conclusions

First-principles calculations based on the density functional theory were performed to investigate the degeneration of the two layers C_3N system with the intercalation of Li and Na atoms. As the calculations show, and we can expect, the degeneration process is directly dependent on the size of the ions. Furthermore, in a hollow site intercalated case, the system is much more stable. The swelling effect shown here is a significant problem during battery operation, charging, and discharging processes. The distance between the layers increases from 3.3376 Å for pure two-layer to 4.8171 Å for Li intercalation, and to 8.1539 Å for Na intercalation. Such a large change in the distance between the layers in the case of Na precludes the use of sodium as the ion, but does not completely rule it out. It all depends on the scale of the battery. Moreover, in the real case we are dealing with an electrolyte, for which the swelling effect may not be a problem. The electrolyte itself fills a certain space. We hope that this research may come closer to discovery of new potential materials in the context of battery electrodes.

Acknowledgments

This research was supported in part by PLGrid Infrastructure.

References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science* **306**, 666 (2004).
- [2] A.P. Durajski, K.M. Gruszka, P. Niegodajew, *Appl. Surf. Sci.* **532**, 147377 (2020).

- [3] A. Khandelwal, K. Mani, M.H. Karigerasi, I. Lahiri, *Mat. Sci. Eng. B* **221**, 17 (2017).
- [4] M. Alidoust, M. Willatzen, A.-P. Jauho, *Phys. Rev. B* **99**, 125417 (2019).
- [5] A.J. Mannix, X.-F. Zhou, B. Kiraly et al., *Science* **350**, 1513 (2015).
- [6] H. Oughaddou, H. Enriquez, M.R. Tchallala, H. Yildirim, A.J. Mayne, A. Bendounan, G. Dujardin, M. Ait Ali, A. Kara, *Prog. Surf. Sci.* **90**, 46 (2015).
- [7] J.-K. Lyu, S.-F. Zhang, C.-W. Zhang, P.-J. Wang, *Ann. Phys. (Berlin)* **531**, 1900017 (2019).
- [8] J. Shah, W. Wang, H.M. Sohail, R.I.G. Uhrberg, *2D Materials* **7**, 025013 (2020).
- [9] S. Yang, W. Li, C. Ye et al., *Adv. Mat.* **29**, 1605625 (2017).
- [10] X. Zhou, W. Feng, S. Guan, B. Fu, W. Su, Y. Yao, *J. Mater. Res.* **32**, 2993 (2017).
- [11] G.-C. Guo, R.-Z. Wang, B.-M. Ming, C. Wang, S.-W. Luo, M. Zhang, H. Yan, *J. Mater. Chem. A* **7**, 2106 (2019).
- [12] G.T. Kasprzak, K.M. Gruszka, A.P. Durajski, *Acta Phys. Pol. A* **139**, 621 (2021).
- [13] R. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, Oxford, 1989.
- [14] P. Giannozzi, O. Andreussi, T. Brumme et al., *J. Phys. Condens. Matter.* **29**, 465901 (2017).