Graphyne as the anode material of magnesium-ion batteries: ab initio study

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(Dated: March 17, 2022)

Graphyne, a single atomic layer structure of the carbon six-member rings connected by one acetylenic linkage, is a promising anode of rechargeable batteries. In this paper, a first-principle study has been carried out on graphyne as a new candidate for the anode material of magnesium-ion batteries, using density functional theory calculations. The main focus is on the magnesium adsorption on graphyne surface. The structural properties such as adsorption height and energy, the most stable adsorption sites, the Band structure and DOS of the pristine graphyne and the Mg-decorated graphyne structures, and energy barrier against Mg diffusion are also calculated. As a consequence of the band structure and DOS of graphyne structures, it is found that the pristine graphyne and the Mg-decorated graphyne structures show a semiconducting nature and metallic behavior, respectively. Moreover, the migration behavior of Mg on graphyne for the main diffusion paths is determined by Nudged Elastic Band (NEB) method.

I. INTRODUCTION

Nowadays, with the acceleration of global energy demands, the depletion of fossil fuels, and their environmental impacts; interest in renewable energies has increased considerably over the last decades. In the meantime, efforts to develop energy storage devices as a renewable energy technology become more prevalent. One of the most popular energy storage system, lithium-ion batteries, have received remarkable attention. A battery is an electrochemical device which converts chemical energy directly into electrical energy and consists of three components, i.e., the anode (negative electrode), the cathode (positive electrode), and electrolyte. During discharge, lithium ions depart from the anode to the cathode through the non-aqueous liquid electrolyte and carry the current which leads to passing electrons around the external circuit to power various systems. When the battery is charging, an external electrical power source make the current to transfer in the reverse direction and lithium ions migrate to the anode across the electrolyt.\textsuperscript{[12]}

Recently, rechargeable batteries have entered our daily life and have been widely applied in portable and telecommunication electronic devices, transportation, and household-type items. Basically, rechargeable batteries have a significant role in the development of electronic devices such as; hybrid electric vehicles, notebook, mobile, flash lights, radios, watches, etc. They became very common because of their high energy density, enhanced rate capabilities, low self-discharging, long cycle life, excellent safety features, and etc. A great deal of attention has been paid to Li-ion battery technologies which are conquering the market, but due to having a better chance of reaching maturity, we decide to apply a different material for this technology.\textsuperscript{[30]}

Since the batteries coming into existence, graphite-based materials have been proposed for anodes. Graphite, the most stable form of carbon, has a layered, planar structure. The carbon atoms in each layer, have been placed in a honeycomb lattice and the individual layers are called graphene. Both graphite and graphene are allotropic forms of carbon. It is well known that graphite has a low capacity and that is not good enough for providing endless needs of the current society. Graphene, a two dimensional (2D) sheet of sp\textsuperscript{2}-hybridized carbon, has a higher capacity than graphite, mainly because lithium can be adsorbed on both sides of graphene, thus lithium has a larger space to diffuse and it can be led to higher rate of diffusion.\textsuperscript{[33]} Graphene has many extraordinary properties which have attracted the attention of all researchers for a while. It is very strong and conducts heat and electricity efficiently.\textsuperscript{[11]} However, nowadays scientists are investigating that “Could graphyne be better than graphene?” Graphyne (Gy), a novel carbon allotrope, is the single atomic layer structure of the carbon six-member rings connected by one acetylenic linkage (-\ce{C≡C−}), which introduces a diverse range of optical and electronic properties. Moreover, the thing that makes graphyne special is the presence of both sp and sp\textsuperscript{2} hybridized carbon atoms. Also, it can be said that graphyne has two different Dirac cones lying slightly above and below the Fermi level which means it is self-doped and naturally includes conducting charge carriers (electrons and holes) without any external doping. Therefore, graphyne is a promising semiconductor which can be used in electronic devices.\textsuperscript{[39]}

In this paper, we have focused on graphyne and Mg-
decorated graphyne-based systems. Magnesium, an inexpensive and environmentally friendly metal with great raw material abundance and good operational safety, is a relatively new option for use as an anode material in rechargeable batteries. (To begin, we examined stability of graphyne by calculating the phonon spectrum using FHI-aims package). Then, we have conducted our study for possible sites of Mg adsorption on graphyne by calculating the adsorption energy and its corresponding adsorption height. Moreover, we examined the electronic structure of graphyne and Mg-decorated graphyne systems at different sites by calculating the band structure and DOS spectrum. Finally, the main target of this work: study for in-plane and out-plane diffusion paths of Mg on a graphyne layer and out-plane diffusion pathway of Mg in bulk graphyne, corresponding energy curves of adsorption sites of Mg on graphyne monolayers, and corresponding transition states (TS); was determined using Nudged Elastic Band (NEB) method.

II. COMPUTATIONAL DETAILS

Our electronic structure calculations and geometry optimizations have been performed in the framework of density functional theory (DFT) by using plane wave pseudo-potential as well as numerical orbital - full potential techniques, implemented in the Quantum Espresso and FHI-aims computational packages, respectively. We used GGA-PBE exchange-correlation functional. The 7×7×1 Monkhorst-pack scheme was used for sampling first Brillouin zone. A vacuum thickness of about 22 Bohr was utilized to avoid interaction of adjacent molecules. Energy cutoffs of 35 Ry and 350 Ry, were used for plane wave expansion of wave functions and electron density. The Nudged Elastic Band (NEB) method, implemented in Quantum Espresso, was also used to determine the reaction path. In this method, a path with the lowest energy is determined for the reaction and then a string of images of the system are created. Finally, the images are connected together through the hypothetical springs with the same spring constant. It results in an energy for each image. In this research, minimum Energy Path was calculated as a function of adsorption sites of Mg on Gy monolayer by considering 59 and 19 images for in-plane and out-plane diffusion and 23 images for diffusion pathway of Mg in bulk graphyne, respectively. The vdW-DF, non-local correlation functional, proposed by Dion et al. utilized to calculate distances between layers and distance between ion and layer.

One of the most important issues in condensed matter physics and in theoretical chemistry is the determination of the reaction path. Many different methods have been presented for finding Minimum Energy Paths (MEPs) and saddle points like the Drag method, the NEB method, the CPR method, the Ridge method, the DHS method, and the Dimer method; which the Nudged Elastic Band (NEB) method was used in this study. In

III. RESULTS AND DISCUSSIONS

To examine graphyne as a reliable anode material of magnesium-ion battery, we not only look at the pristine graphyne and its properties, but also focus on the adsorption behavior of the magnesium atoms onto the graphyne surface. We first relaxed a single-layer graphyne, which is displayed in Fig.2. The bond length between the sp- and sp²-hybridized C atoms are 1.22 (Å) and 1.42 (Å), respectively and the C–C bond length that connect sp- and sp²-hybridized C atoms is 1.39 (Å) which is in agreement with other researchers.  

A. Mg adsorption on graphyne surface

To survey the adsorption behavior, we considered the most stable locations for Mg decoration in graphyne. The Mg atom can adsorb above the centers of large and small hexagons which consisting of 12 and 6 carbon atoms, respectively and they are denoted as H- and h-sites here-
after. Another adsorption site for Mg named H-beside-site, H-bond-site, and h-bond-site in which Mg atom stands right above one of the corners of large hexagons, right above one of the carbon bonds of large hexagons, right above one of the carbon bonds of small hexagons, respectively. The different Mg-decorated graphyne structures are shown in Fig. 2.

We turn to investigate the electronic properties of graphyne with Mg atom in different positions. Table I summarizes the calculated binding energy, \( E_b \), the distance between Mg and graphyne, \( d_{Mg-graphyne} \), and the charge transfer of the Mg atom, where \( E_b \) and \( d_{Mg-graphyne} \) are defined by equation (1) and van der Waals correction of Mg atom in H-site structure, H-bond-site and h-site structures are 4.15(Å), 4.02(Å), and 4.07(Å), respectively, while in the case of the H-site structure, the distance between Mg and graphyne decreases to 1.34(Å). Among the four structures, the H-site is the most favorable due to more negative binding energy in comparison to others. The charge transfer from Mg atom to graphyne, is calculated by Bader analysis. The results in Table I show that as the Mg distance decreases the charge transfer increase. Mg atom in H-site structure transfers 1.35 electrons to the substrate and More than others. Which would be responsible for the greater negative binding energy and consequently more stable structure.

### Table I. Calculated binding energies \( E_b \), distances between Mg and graphyne \( d_{Mg-graphyne} \) and the charge transfer of Mg atom

| Structures       | \( E_b(\text{eV}) \) | Distance(Å) | \( \Delta Q[\text{e}] \) |
|------------------|---------------------|-------------|-----------------|
| h-bond-site      | -0.47               | 4.15        | 0.07            |
| H-bond-site      | -0.48               | 4.02        | 0.08            |
| h-site           | -0.47               | 4.07        | 0.07            |
| H-site           | -0.87               | 1.34        | 1.35            |

\[
E_b = (E_{Gy} + nE_{Mg} - E_{Mg-Gy})/n \quad (1)
\]

To approach reality, a supercell containing two graphyne layers with an AB stacking sequence was also considered. The interlayer spacing in graphyne was set to be 3.45 (Å), which has been recognized in the range of the most stable interlayer distances. The top view of bulk graphyne with an AB stacking sequence is shown in Fig. 3a. The Mg atom can be intercalated into the bulk graphyne in two sites, which are named HH- and hH-sites. In HH-site the Mg atom is take placed between centers of large hexagons of two adjacent layers and in hH-site the Mg atom is placed between centers of a small hexagon and a large hexagon of two adjacent layers. The binding energy of HH- and hH-sites are ... and ..., respectively. The corresponding adsorption height for HH-site is about 1.8 (Å), in which the Mg atom is nearly in the middle of the spacing of the two adjacent layers. In the hH-site, Mg atom is closer to the large hexagon with a distance of 1.24 (Å). Comparison reveals that the intercalated Mg prefers to occupy an H-site rather than other sites, due to its larger binding energy. It is worth noting that due to the existence of a van der Waals force between the Mg atom and the graphyne surface, the van der Waals effects have been considered in the above-mentioned calculations.

### B. Electronic properties

The band structure and density of state (DOS) have been calculated to study the electronic properties of pristine graphyne and Mg adsorbed graphyne layer systems. The band structure, and Dos of the pristine graphyne and the different Mg-decorated graphyne structures are shown in Fig. 2. For pristine graphyne, the band structure and Dos imply a semiconducting behavior with the direct band gap of 0.358 (eV) due to the same location of the valence band maximum (VBM) and conduction band minimum (CBM) of graphyne. This gap is in good agreement with the results of 0.38 (eV) for Na-decorated graphyne batteries from other DFT calculations. Moreover, it can be seen from the band structure and Dos of the Mg-decorated graphyne structures that there is a comparable downward shift of the conduction band for each structure (and, alternatively, an upward shift of the Fermi level), indicating that the Mg adsorption makes graphyne metallic. These results are consistent with the density of state of all structures considered in this paper. It is noteworthy that the downward shift of the conduction band for H-site is the highest among all structures considered in this research.

The calculated band structure and density of state of graphyne by replacing Mg atom on the top of the large and small hexagons (H and h sites) are presented in Fig. 2 which exhibit an overlapping between conduction band and Fermi energy. All the other Mg-decorated graphyne structures show the same metallic nature but the amount of overlapping between the conduction band and Fermi energy is different.

In order to determine the constituents of the electronic band, the projected density of states was calculated for graphyne with different Mg-decoration. The state near the Fermi level are mainly dominated by Mg s orbital in h-bond-site, H-bond-site, and h-site. Decreasing distance between Mg and substrate in H-site structure results in the Mg s orbital contribution reduction in the Fermi state. It is found that the Mg p and s orbitals have influenced in Fermi level, But the graphyne states play a very important role in the Fermi state. The charge transfer on the substrate in this decoration is extremely
FIG. 2. The band structure of a) Gy, b) h-bond-site, c)H-bond-site, d) h-site and e) H-site. The Optimized structure of single-layer graphyne labeled with prime. The blue and red spheres represent C atoms and Mg atom, respectively.

more than others.

There is a large difference in electronegativity between Mg and C atoms which cause a charge transfer from Mg to C atoms and thus the metallic behavior can be seen, that is an important characteristic for some applications such as electrode materials in rechargeable batteries.

C. Mg diffusion in Graphyne

Considering the significance of Mg mobility on graphyne monolayer, the diffusion path is calculated on the way to the most stable adsorption sites using the Nudged Elastic Band (NEB) method. We investigated Mg migration behaviors for two main diffusion paths; in-plane diffusion paths (h1-site to H1-site, H1-site to H2-site, H2-site to h2-site) and out-plane diffusion paths (across the hollow of H-site and h-site) as depicted in Fig. 3 respectively. Since the calculation of energy curves is meaningful and very deterministic on battery applications, the corresponding Minimum Energy Paths (MEPs) are also shown as a function of adsorption sites of Mg on graphyne monolayer and two layers in Fig. 5

The results from Fig. 4(a) indicate that the activation energy barrier of Mg diffusion along the h-site to H-site direction is identified to be 0.072 (eV) and the transition state (TS) is located on the image. 9; where is near the top of the midpoint of the C(sp²)-C(sp²) bond between two adjoining hollows of large and small hexagons but more leaning to the large hexagon. Moreover, Mg migration between two neighboring H-site is as high as 0.835 (eV), more than that in h-site to H-site diffusion path, and it can be seen that the transition state (TS) is specified near the top of midpoint of the C(sp²)-C(sp²) bond between two adjacent hollows of large hexagons; where is known by image.30. As the reaction pathway is followed, there is a high energy barrier of about 0.783 (eV) for Mg diffusion along the H-site to h-site path; which is reside on image.51 and represent the energetic favorability of the H-site over the h-site. In addition, the h1-site to H-site diffusion path with the lowest energy barrier of about 0.072 (eV) is mainly dominated in the in-plane Mg migration on Gy.

In the following, the energy profiles of two typical out-plane diffusion paths are also studied, which can be seen in Fig. 4(b) and 4(c), respectively. In out-plane diffusion paths Mg migrates from one side of a graphyne layer to another side along the direction perpendicular to the graphyne plane. The energy barrier for Mg diffusion through a large and small hexagon is about 0.32 (eV) and 15.68 (eV), respectively. Therefore, Mg can easily migrate through the large hexagon by overcoming a relatively small energy barrier of 0.32 (eV). Moreover, it can be seen that the out-plane diffusion of Mg across the small hexagon is energetically and kinetically prohibited because of such a high energy barrier. Eventually, the large hexagon (H-site), formed by the sp²- and sp-hybridized C atoms in graphyne, is recommended for both Mg adsorption and out-plane Mg migration. In addition, according to Fig. 5(c) the energy barrier of Mg diffusion along the Hh-site to hH-site and hH-site to HH1-site are calculated to be 0.927 (eV) and 1.001 (eV), respectively, whereas that from HH1-site to hH-site are more than 1.001 (eV). Furthermore, there is a large barrier energy of 1.829 (eV) from HH1-site to HH2-site, which is energetically unfavorable. But the energy barrier along HH2-site to HH1-site is about 0.284 (eV), that is related to the reduction of the density of graphyne layers in this area.
FIG. 3. The schematic drawings of a,b) in-plane diffusion paths (h1-H1-H2-h2) Side image and image from above and two out-plane diffusion paths c) across the hollow of H-site d) across the hollow of h-site

IV. CONCLUSION

In this work, density functional calculations were employed to systematically investigate the pristine graphyne and Mg-decorated graphyne structures as a new anode material of magnesium-ion batteries, using Quantum Espresso package. The obtained results from calculated adsorption energy and adsorption height determined the most stable adsorption sites of magnesium on graphyne. Moreover, exploring on the DOS and band structure of the pristine graphyne and Mg-decorated graphyne structures, it was observed that the Mg adsorption makes graphyne metallic. we calculated a direct band gap of 0.358 (eV) for pristine graphyne, which is in good agreement with the results of 0.38 (eV) for Na-decorated graphyne batteries from other DFT calculations[8]. Also, we determined the Mg-migration behaviors on graphyne monolayer on the way to the most stable adsorption sites for two main in-plane and out-plane diffusion paths, in addition, an out-plane diffusion pathway of Mg in bulk graphyne along the Hh-hH-HH1-HH2 direction, using Nudged Elastic Band method. The activation barrier of this process for in-plane diffusion path along h1-H1, H1-H2, and H2-h2 directions are 0.072 (eV), 0.835 (eV), and 0.783 (eV), respectively. Besides, the energy barrier for Mg out-plane diffusion through H-site and h-site is about 0.32 (eV) and 15.68 (eV), respectively. Furthermore, for diffusion of Mg in bulk graphyne along the Hh-hH, hH-HH1, and HH1-HH2 paths, energy barriers are calculated to be 0.927 (eV), 1.001 (eV), and 1.829 (eV), respectively.

In summary, investigation of details about Mg intercalation and diffusion into graphyne monolayer is highly desirable to shed light on this topic and to achieve the better understanding of battery technology.

V. ACKNOWLEDGMENTS

The authors gratefully acknowledge the Sheikh Bahaei National High Performance Computing Center (SBNHPCC) for providing computing facilities and time. SBNHPCC is supported by scientific and technological department of presidential office and Isfahan University of Technology (IUT).

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FIG. 4. Mg migration behaviors a) in-plane diffusion paths (h1-H1-H2-h2) and two out-plane diffusion paths b) across the hollow of H-site c) across the hollow of h-site

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FIG. 5. The schematic drawings of a,b) out-plane diffusion pathway of Mg in bulk graphyne (Hh-HH-HH-HH) Side image and image from above and b) the corresponding energy profile as a function of adsorption sites.

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