Thermodynamics and kinetics of 2D g-GeC monolayer as an anode materials for Li/Na-ion batteries

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**HIGHLIGHTS**
- Graphene is designed as anode materials for Li/Na-ion batteries.
- Thermodynamics and kinetics of g-GeC as an anode is explored by DFT calculations.
- The Li/Na-intercalation into g-GeC can offer a theoretical capacity of 633 mA h/g.
- New rational design of Ge/C compounds as novel anode materials is reported.

**GRAPHICAL ABSTRACT**

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**ABSTRACT**

Development of high capacity anode materials is one of the essential strategies for next-generation high-performance Li/Na-ion batteries. Rational design, using density functional theory, can expedite the discovery of these anode materials. Here, we propose a new anode material, germanium carbide, g-GeC, for Li/Na-ion batteries. Our results show that g-GeC possesses both benefits of the high stability of graphene and the strong interaction between Li/Na and germanene. The single-layer germanium carbide, g-GeC, can be lithiated/sodiated on both sides yielding Li\textsubscript{2}GeC and Na\textsubscript{2}GeC with a storage capacity as high as 633 mA h/g. Besides germagraphene’s 2D honeycomb structure, fast charge transfer, and high (Li/Na)-ion diffusion and negligible volume change further enhance the anode performance. These findings provide valuable insights into the electronic characteristics of newly predicted 2D g-GeC nanomaterial as a promising anode for (Li/Na)-ion batteries.

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1. Introduction

In recent decades, new technologies have grown rapidly and our daily lives are heavily influenced by energy storage systems (ESSs). From electric- and hybrid-vehicles to large smart grids and various electronic-devices, energy storage technologies play a strategic role in providing efficient ways to transmit/commercialize energy from sustainable alternatives. In particular, Lithium-ion-based rechargeable batteries (LIBs), represent an efficient energy storage system [1–3]. However, due to the rising high-cost of lithium as well as its growing scarcity, the emphasis has shifted to low-cost Sodium-ion batteries (NiBs) [4,5]. The rational design of the most suitable anode materials has focused on two-dimensional materials. Up to now, graphene is the most widely used anode material commercially, in spite of its limited specific capacity of 372 mA h g⁻¹ in LIBs. The difficulty of Na-ion intercalation between the graphite layers due to its large atomic radius compared to that of Li-ion makes it difficult as an electrode in Na-ion-based batteries [6–9]. Similar is the case with 2D Single elemental 2D materials such as silicene [10–13], germanene [12,14], stanene [12,15], phosphorene [16], and borophene [17]. Electronic and mechanical properties, efficient transport of metal-ions from layer-to-layer, availability of areas for better ionic adsorption, fast oxidation/reduction surface reactions, high electronic-mobility, ability to build heterostructures, and seamless integration into systems are critical factors for battery performance. In this respect, the design and synthesis of novel 2D materials for energy storage represent a high priority and a key challenge.

Given its large Li-storage capacity and wide Li-diffusion rate, germanium has been studied as a standard alloy-like anode material for Li-ion batteries [18,19]. Studies, based on first-principle calculations, indicate that the germanium materials can be used as a potential negative electrode for Na-ion batteries [20,21]. This is because of its high thermodynamic coupling forces, the moderate volume expansion during Na-insertion, and the ability to form NaGe chemical formula with a theoretical specific capacity of about 369 mA h g⁻¹ [20–24]. However, experiments have shown that the Na-insertion in crystalline Ge is very small due to a significant diffusion-barrier of Na-ions into the Ge crystal structure [25]. The higher atomic radius of Na⁺ versus Li⁺ (0.98 vs 0.68 Å) is responsible for the greatly increased activation energy for migration between the different adsorption sites in the pristine materials (about 0.51 eV in the case of Li-ion versus 1.5 eV in the case of Na-ion) [26,27]. In addition, poor electrical-conductivity and large volume expansion that can reach as high as ~300% for a fully lithiated and sodiated process (Li₂Ge and Na₄Ge) [28,29] stand in the way of the practical application of germanium as an anode material in both Li/Na-ion batteries. To overcome these fundamental limitations, Ge/C composites [30–33] have been recently considered as they offer many advantages such as great stability, high electric- and ionic-conductivity of graphite-based nanomaterials as well as good electrochemical stability due to stable sp²-electronic configuration. In addition, the metallic behavior of graphene provides an excellent electrical conductivity while the hexagonal honeycomb structure allows for low diffusion of Li/Na-ion as well as strong intrinsic interactions between Li/Na and Ge atom offered by Germanium.

Mortazavi et al. have described in detail the interaction between Li/Na-ions and silicon, germanene, and stanene monolayers and reported that the adsorption energy of (Li/Na) ion is significantly greater in these structures compared to that of graphene [32]. Germanene is a 2D-alto- tropo of bulk Germanium (b-Ge) exhibiting a 2D-honeycomb hexago- nal structure similar to that of graphene. Due to higher layer-to-layer coupling compared to planar 2D structure, it has a deformed phase configuration [34]. Recently, it has also been reported that Li-ion has a much higher binding energy to germanene than to graphene, with high electron conductivity and therefore a greater Li-storage is expected for monolayer and bilayer germanene [14]. However, both 2D silicene and germanene monolayers are not stable under normal conditions and the experimental condition for the growth of germanene is very strict, which makes germanene not applicable in real battery, and do not address a solution to solve the fundamental challenges of Ge-based anode materi- als [35,36,76]. In addition, Ge-carbon nanotube composite [31], Germanium/Carbon nanostructures [33], and sandwich-structured C/Ge/graphene nanocomposite [37] have been proposed as alterna- tive negative-electrode materials for lithium-ion batteries.

Density functional theory (DFT) based calculations have predicted ergamaphene (g-GeC) to have a planar structure [38–42] like 2D graphene with Ge-atoms partly (50%) replacing the C-atoms in the graphene monolayer. It exhibits greater structural, thermodynamic, and mechanical stability, and can be developed through several synthesis methods, including Chemical Vapor Deposition (CVD) [43], Activated-Reactive-Evaporation (ARE) process [44], and more recently, Plasma-Enhanced Chemical-Vapor-Deposition (PE-CVD) [45], as well as, radio frequency magnetron sputtering method [46].

According to the above-mentioned computational and experimental literatures, DFT were employed to explore the applicability of germanium carbide monolayer as a promising anode material for Li/Na-ion rechargeable batteries. Initially geometrical, stability, and electronic properties of pristine monolayers were investigated. Then, the binding energies of Li and Na at different available adsorption sites were computed for single-layer graphene, germanene, and g-GeC. The electronic properties after a single Li and Na adsorb on the g-GeC monolayer (including band structure and total/partial-density-of-state), In addition, the (Li/Na)-diffusion barriers in the case of g-GeC mono- layer were investigated. Finally, different Li, and Na concentrations is also used in order to estimate the open-circuit voltage and the theoretical specific capacity of g-GeC as anode for Li/Na-ion batteries.

2. Computational methods

Density functional theory with the Projector Augmented Waves (PAW) method [46] was used throughout our calculations. The Plane-Wave Self-Consistent Field or PWscf package implemented in the Quantum ESPRESSO was employed [47]. The exchange-correlation potential was treated within the generalized-gradient-approximation due to Perdew-Burke-Ernzerhof (GGA-PBE). Plane-waves with a kinetic energy cutoff of 500 R y were used to describe the wave function. According to the Monkhorst-Pack model [48], All geometrical structures were optimized using 15 × 15 × 1 k-points grid and the structural parameters were optimized with the forces and energy converged to 0.01 eV/Å and to 10⁻⁵ eV/Å respectively. The effect of van der Waals interaction has been described by using the empirical correction in the Grimme method i.e. zero damping DFT-D3 during the calculations [49]. To recheck the energetical stability of our structure, the cohesive energy was computed by:

$$E_{coh} = E_{tot} + E_C + E_{GeC}$$

The most stable binding sites of Li and Na-atom on the g-GeC surface were determined based on locating Li and Na atoms across the possible binding sites and evaluating the resulting adsorption energies, $E_d$, defined as follow:

$$E_d = E_{Li/Na@GeC} - E_{GeC} - E_{Li/Na}$$

Here, $E_{Li/Na@GeC}$ refers to the energy of Li/Na@GeC, $E_{GeC}$ represents the energy of the pristine monolayer, and $E_{Li/Na}$ refers to the energy of a Li and Na atom in the bulk system. From the definition, the positive values of adsorption energy refer to the repulsion (no adsorption). And a negative value denotes attraction, which is an indicator that adsorption is privileged.

From a practical standpoint, the open-circuit voltage plays one of the most crucial roles in characterizing the anode materials of Li and Na-based rechargeable batteries. The average adsorption energies were derived with growing Li and Na-atoms on both sides of the g-GeC
surface. Throughout the charge/discharge operation, the anode/cathode reacts electrochemically in a reversible process. On the anode side, the typical half-cell reaction vs (Li)/(Li)\(^+\) and (Na)/(Na)\(^+\) is:

\[
\text{xLi}^+ + \text{xe}^- + \text{Li}_x\text{GeC} \rightleftharpoons \text{Li}_x\text{GeC}
\]

\[
\text{xNa}^+ + \text{xe}^- + \text{Na}_x\text{GeC} \rightleftharpoons \text{Na}_x\text{GeC}
\]

The average adsorption energy \(E_{\text{avg}}\) were calculated using the formula

\[
E_{\text{avg}} = \frac{E_{\text{Li/NaGeC}} - E_{\text{GeC}} + xE_{\text{Li/Na}}}{x}
\]

Another important factor to be considered in order to judge the high concentration amount of Li/Na-storage is sequential adsorption strength defined as follow:

\[
E_{\text{seq}} = E_{\text{(Li/Na)GeC}} - E_{\text{GeC}} - xE_{\text{Li/Na}}
\]

where, \(E_{\text{(Li/Na)GeC}}\) and \(E_{\text{Li/NaGeC}}\) refers to the total energy of 2D g-GeC material with \((n+1)\)Li/Na and nLi/Na adsorbed, respectively. The lower and smaller sequential adsorption energy compared to the cohesive energy of Li and Na atom in the bcc reference state means that the behavior of Li/Na-adsorption is thermodynamically stable.

Secondary battery voltage represents a key factor that is proportional to the battery’s energy storage. According to earlier studies, it can be approximated using the following formula and assuming that both changes in volume at constant pressure (\(\text{P}AV\)) and entropic contribution (\(\text{T}\Delta S\)) are negligible [50–53].

\[
V_{\text{OCV}} = -\frac{E_{\text{coh}}}{e}
\]

The theoretical capacity of g-GeC monolayer as anode materials for Li and Na-ion batteries is computed by:

\[
C_{\text{F}} = \left(\frac{\text{mA}}{\text{g}}\right) = \frac{x \times F}{M_{\text{GeC}}}
\]

Here, \(x\), \(F\), \(M_{\text{GeC}}\) are the concentration of (Li/Na)-ions adsorbed on 2 \(\times\) 2 super-cell of g-GeC monolayer, the Faraday constant, and the molecular weight of 2 \(\times\) 2 super-cell, respectively.

To investigate the diffusion pathways of Li and Na-atoms on the g-GeC surface, the CI-NEB [54,55] approach is employed by using 10 images from the starting to the ending most stable adsorption site. The temperature-dependent molecular transition rate was evaluated using the Arrhenius equation defined as following [56]:

\[
D = e^{-\frac{E_{\text{coh}}}{k_{\text{B}}T}}
\]

Here, \(D\) represents the diffusion barrier obtained from the diffusion of (Li/Na)-ion on the g-GeC surface, \(k_{\text{B}}\) and \(T\) are Boltzmann’s constant and the temperature, respectively.

To further describe the interaction that occurs between the Li/Na atoms and g-Ge monolayer during the insertion operation, the charge transfer was evaluated according to Bader’s charge algorithm. The difference charge density was computed within the unit (\(|e|/\AA^2\)) according to the formula:

\[
\Delta \rho = \rho_{\text{Li/NaGeC}} - \rho_{\text{GeC}} - \rho_{\text{Li/Na}}
\]

where \(\rho_{\text{Li/NaGeC}}\) denote the electron-charge density of on the hollow site in 3 \(\times\) 3 supercell, \(\rho_{\text{GeC}}\) of the pristine system and \(\rho_{\text{Li/Na}}\) of (Li/Na)-atom at the favorable adsorption site. And finally, the VESTA [57] was used for the posttreatment analyses. Further information regarding methodologies can be found in our recent studies [74,75].

3. Results and discussion

3.1. Structure, stability, and electronic properties of g-GeC monolayer

Typically, 2D-GeC materials derived from their bulk-GeC exhibit two different phases a planar and a deformed phase. In the first one, all Ge- and C-atoms are on the same plane and in the second some atoms protrude upward. In order to find the preferred structure of g-GeC monolayer, the energetic stability for both structures is investigated by calculating the cohesive energy. Our finding shows that the planar phase is the preferred one with \(E_{\text{coh}}\) lower by 0.3 eV. 2D g-GeC monolayer exhibits hexagonal unit-cell similar to that of graphene, with the hexagonal-rings containing three Ge and three C atoms. Both Ge and C-atoms are sp \([2]\)-hybridized forming a 3D-network. Fig. 1a illustrates the top view of a 2 \(\times\) 2 \(\times\) 1-supercell of the g-GeC monolayer with the projected electron charge density (ECD). The equilibrium lattice-parameter, Ge-C bond-length, and bond-angle of optimized g-GeC are found to be \(a = b = 3.24\ \text{Å}\), \(d\ \text{Ge-C} = 1.87\ \text{Å}\), and 120°, respectively, in agreement with earlier works [41,42,58].

Fig. 1c and d elucidate the electronic properties including the band-structure and associated total/partial density of states (DOS) for g-GeC monolayer. Based on the band structure plot, it can clearly be observed that g-GeC monolayer exhibits a semiconducting character with a direct band-gap at the K-point of 2.10 eV at the GGA-PBE level and 2.90 eV using HSE06 hybrid functional. These results agree with previous studies [41,42,58,59]. Additionally, based on the total and partial DOS plots, it can be clearly seen that the major contribution to VBM and CBM comes from the p-orbital of Ge and C atoms. The electron charge density of g-GeC monolayer, as presented in Fig. 1a, indicates an e-rich region around the C-atoms and an e-poor region around the Ge-atoms Thus, the charge is transferred from the more electronegative C-atom (2.5) to the less electronegative Ge-atom (1.8). According to Bader-charge analysis [60], the Ge-atom loses 3.88 [e] electron per atom and C-atoms gain 3.88 [e] electron per atom, which is consistent with the difference charge density shown in section 3-5.

Before moving to a detailed study of the feasibility of GeC as a battery anode, it is important to verify the dynamic and thermal stability of the host monolayer. We performed the phonon dispersion calculation and AIMD simulation. Fig. 1b shows the phonon dispersion pattern along the k-vectors with high symmetry. The maximum frequency value corresponded to 898 cm\(^{-1}\), without any imaginary or negative frequencies in the first Brillouin zone, indicating the dynamical stability of the g-GeC structure. The thermal stability of the pristine structure is also tested with molecular dynamics simulations at high temperatures using DFT/GGA theory and the PBE exchange-correlation functional, making use of NVT ensembles as implemented in VASP code. These simulations were run for 10 ps at 800 K in (5 \(\times\) 5)-supercell. No Ge-C bond breaking is seen, indicating the higher degree of stability of this structure. The results are given in Fig. 1e. In addition to the snapshot, we can also see that free energy is well converged in the given period for all the temperatures. This confirms the thermal stability of the structure.

3.2. (Li/Na)-ion adsorption on a single layer graphene and germanene

Before analyzing the Li/Na ion adsorption capability of GeC, it is crucial to study the (Li/Na)-ion adsorption in its parent structures, namely, graphene and germanene monolayers. 2 \( \times\) 2-supercell of graphene and germanene monolayer containing 8 C-atoms (as shown in Fig. 2a) was used to calculate the single (Li/Na)-ion adsorption. In the optimized graphene supercell (of lattice constants \( \sim 4933\ \text{Å}\)), each C-atom is bound to three other carbon atoms through \(\text{sp}[2]\)-hybridization. The C-C bond length and C-C-C bond angle are 1.421 Å and 120°, respectively. In germanene, the optimized lattice constant, buckling height (d), Ge–Ge bond-length, and bond-angle are, respectively, 8.036 Å, 0.672 Å, 2.4382 Å, and 112.229°, which agree with the previous study [12,36,40,61,62]. As illustrated in the upper panel of Fig. 2a, we
Fig. 1. (a) Top view of \((2 \times 2)\)-supercell of relaxed 2D germagranphene (g-GeC) with the projected electron charge density, (b) the phonon dispersion pattern along the k-vectors with high symmetry, (c–d) Band structure and total and partial density of state, respectively. The fermi-level is set at zero, (e) The top-snapshots with the corresponding variation of the total-energy between 0 and 10 ps during the ab-initio molecular dynamics (AIMD) simulations at 800 K.

Fig. 2. (a) Top view of \((2 \times 2)\)-supercell of optimized 2D graphene (upper panel) and germanene (lower panel), with considered representative adsorption sites. (b–c) Geometries of top- and side-view after optimization of the highest (Li/Na)-concentration of germanene \((\text{Li}_8\text{Ge}_8\) and \(\text{Na}_8\text{Ge}_8\)). The adsorption sites T, H, and B correspond to Li/Na-ion adsorption at the top, hollow, and bridge sites, respectively in the case of graphene monolayer. For germanene monolayer \(T_1\) and \(T_2\) refer to top sites above higher-plane Ge- and lower-plane Ge-atoms, respectively.

Table 1
The (Li/Na)-ion adsorption energies and heights at the different graphene (germanene) adsorption sites; heights correspond to the vertical distance between (Li/Na)-ion and monolayers.

| Sites | H-site | T-site | B-site | H-site | T1-site | T2-site | B-site |
|-------|--------|--------|--------|--------|---------|---------|--------|
| Li    | \(E_{ad}\) (eV) | -1.374 | -1.055 | -1.068 | -2.22   | -1.97   | -1.70  | -1.96  |
|       | Height (Å)   | 1.692  | 1.937  | 1.908  | 1.58    | 2.09    | 1.84   | Move to T1-site |
| Na    | \(E_{ad}\) (eV) | -0.702 | -0.646 | -0.654 | -1.53   | -1.36   | -1.24  | -1.35  |
|       | Height (Å)   | 2.326  | 2.568  | 2.526  | 2.18    | 2.44    | 2.19   | Move to T1-site |
have considered symmetrically three most possible distinct binding sites, namely, H-site (top of hexagon ring), T-site (top of carbon/germanium atom), and B-site (in between two carbon/germanium atoms) for (Li/Na)-ion adsorption. The T-site for germanene monolayer is further distinguished as T1- and T2-sites due to the high symmetry of the g-GeC monolayer. H-site refers to the top of the GeC3-hexagon while T1 and T2 sites refer to as the top of the carbon and the germanium atom, respectively. Exothermic behavior of (Li/Na)-ion adsorption on the graphene monolayer is confirmed with the negative adsorption energy, as shown in Table 1. The most favorable adsorption site for both sides of the graphene monolayer is the H-site with adsorption energy of −1.374 eV and −0.702 eV, respectively, for Li-ion and Na-ion. The bond distance of adsorbed (Li/Na)-atom from graphene monolayer is ~1.692 Å for Li-atom and ~2.326 Å for Na-atom, which is consistent with the larger atomic radius of the Na-atom. Similarly, the lowest energy adsorption site in germanium monolayer is H-site with adsorption energy of −2.22 eV for Li and −1.53 eV for Na adsorption, which is comparable to the previous theoretical calculations [14,63]. Lower adsorption energy of the germanium monolayer suggests that it is a better host for Li/Na atoms. Similarly, the lowest energy adsorption site in germanium monolayer is H-site with adsorption energy of −2.22 eV for Li and −1.53 eV for Na adsorption, which is comparable to the previous theoretical calculations [14,63]. Lower adsorption energy of the germanium monolayer suggests that it is a better host for Li/Na atoms. The most suitable adsorption site for full (Li/Na)-concentration is H-site, as indicated in Fig. 2 b and c. Buckling height (d_{buckling}) of pristine germanene monolayer increases from 0.69 Å to 1.29 Å with eight Li atoms adsorbed and 1.06 Å with eight Na-adsorbed. Consequently, the bond-length is increased from 2.438 Å to 2.589 Å/2.562 Å in Li8Ge8/Na8Ge8, but the bond-angle is decreased from 112.23° in germanene to 102.91°/105.38° after adsorption of eight (Li/Na)-atoms. These results indicate that (Li/Na)-ion adsorption enhances sp[3]-hybridization, which may trigger crystalline-germanium formation [24,64], leading to an unstable anode material [36,65].

### 3.3. Single (Li/Na)-ion adsorption on g-GeC monolayer

Although strong interaction of alkali ion with germanene monolayer will favor increasing Li/Na atoms adsorption compared to graphene monolayer, germanene is unstable under ambient conditions (T = 300 K and P = 5 × 10^-7 bar) [36,65]. To have the benefit of both structural stability of graphene and strong (Li/Na)-host interaction of germanene, it is appropriate to consider a combination of both monolayers, such as germanographene, g-GeC. This will benefit from both C and Ge chemistry with similar crystal structures. Fig. 3a shows that there are three possible adsorption sites (H, T1, and T2) due to the high symmetry of the g-GeC monolayer. H-site refers to the top of the GeC3-hexagon while T1 and T2 sites refer to as the top of the carbon and the germanium atom, respectively. Calculated adsorption energies for different sites are shown in Table 2. Adsorption energy trend for Li is H < T2 < T1 and for Na, it is H < T1 < T2. Specifically, in both cases, H-site is energetically the most favorable site as observed in graphene and germanene monolayer. The distance of the adsorbed Li and Na-atom from the host layer is 1.59 Å and 2.49 Å, which is consistent with the atomic radius of Li (182 p.m.) versus Na (227 p.m.).

In order to better elucidate the (Li/Na)-adsorption phenomena on the g-GeC surface and to know the critical adsorption distance, we moved the (Li/Na)-atom vertically from the germanographene surface. Modification in potential energy as a function of the distance of the (Li/Na)-atom from the g-GeC surface is shown in Fig. S3 in SI. It is observed that the energy remains constant at a distance greater than ~9 Å, which means (Li/Na)-atom is completely non-interactive with the g-GeC monolayer. On the other hand, the total energy increases significantly at a distance less than ~7 Å, which indicates the optimal distance at which Li/Na atoms interact with the g-GeC monolayer.

Adsortion energy as a function of (Li/Na)-concentration in GeC host is illustrated in Fig. 4a. The fully lithiated/sodiated configurations of g-GeC monolayer should satisfy the following criteria: a) this phase should have the highest possible (Li/Na)-concentration; b) Negative values of the adsorption energy which implies the capability of more Li/Na-storage in the anode, c) stable structure upon full lithiation and sodiation (the structure should exhibit no-reversible deformation). The top and side views of optimized (Li/Na)-adsorbed structures on the g-GeC monolayer at the highest-concentration (8-Li/Na adsorbed on both

| Adsorption-sites | H-site | T1-site | T2-site |
|------------------|--------|---------|---------|
| Li E_{ad} (eV)   | −1.40  | −1.01   | −1.04   |
| Height (Å)       | 1.592  | 2.136   | 2.138   |
| Na E_{ad} (eV)   | −0.41  | −0.33   | −0.28   |
| Height (Å)       | 2.49   | 2.75    | 3.19    |

**Table 2**

The (Li/Na)-ion adsorption energies and heights at the different germanographene sites. Adsorption heights correspond to the vertical distance between (Li/Na)-ion and germanographene.
atom (of concentration, x = 0.1111) is about \(-0.202 \text{ eV}/-0.18 \text{ eV}\), respectively. At the beginning of the lithiation process, as the Li-concentration increases to 0.5, the adsorption energy decreases. This is due to higher repulsion between neighboring Li-atoms. After that, when the Li-concentration increases beyond 0.5, a progressive increase in Li-adsorption energy is observed, which is accompanied by structural modifications of the g-GeC monolayer from planar to buckled phase at the fully lithiated and sodiated state (x = 2.0). The fully sodiated and lithiated state x = 2.0 where both sides of the system are totally covered, with an average adsorption energy of \(-1.554 \text{ eV}\) for Li2GeC and \(-0.283\text{ eV}\) for Na2GeC. In order to verify the energetic stability of the fully lithiated/sodiated configurations and obtain the theoretical Li/Na-storage capacity, we computed the sequential adsorption energy \(E_{\text{Seq}}\) for 8Li/Na adsorbed on both side of the host material surface and the results are \(-3.052\text{ eV}\) for Li2GeC and \(-1.26 \text{ eV}\) for Na2GeC, greater as compared to the cohesion energy of Li/Na-metal (1.82/1.113 eV) which indicates that the Li/Na-adsorption is energetically favorable and Li/Na-intercalation is allowed. Additionally, it is obtained that in the fully lithiated and sodiated state, the g-GeC with planar structure transforms to a buckled phase (Fig. 3b and c), which can enhance charge transfer as well as decrease the distance between (Li/Na)-atoms and the GeC surface. With these fully lithiated/sodiated concentrations, g-GeC monolayer exhibits a Li-ion and Na-ion theoretical storage-specific capacity of 633 mA h/g. In addition, the molecular dynamic stability of the fully lithiated/sodiated systems were investigated by AIMD simulations at the temperature of 800 K for 10 ps The top and side view of the Li2GeC/Na2GeC systems captured after the MD simulation shows no broken bonds as illustrated in Fig. S3 in SI, thereby supporting the thermal stability of both systems Li2GeC/Na2GeC.

Our predicted theoretical specific capacity is comparable to that of previously reported 2D anode materials. For instance, the theoretical specific capacity of 633 mA h/g for Li-ion batteries is very close to that of GeP3 (648.0 mA h/g) [64]. This is nearly double of the value for commercial graphite (375 mA h/g) [11], and higher than that in the h-BAs (522.08 mA h/g) [67], phosphorene (433 mA h/g) [68], InP2 (258.1 mA h/g) [69]. Similarly, the predicted specific capacity of Na-ion batteries host on g-GeC monolayer is 633 mA h/g, which is larger than that of several reported anode materials for Na-ion, such as, h-BAs (522.08 mA h/g) [67], InP3 (258.1 mA h/g) [69], and 2D Borophene (504 mA h/g) [70]. Fig. 4b shows that increase in (Li/Na)-ion concentration in g-GeC monolayer from Li0.25GeC to Li2GeC (Na0.25GeC to Na2GeC), lowers the open-circuit voltage from 1.39 to 0.19 V for Li-ion and from 0.24 to 0.04 V for Na-ion batteries. This much lower value of open-circuit voltage suggests the suitability of g-GeC as anode materials. Additionally, its high specific capacities and operating voltage with a higher energy density further suggest it as a promising anode material for both LIBs and SIBs.

### 3.4. The cycling and rate performance of germagraphene (g-GeC) as anode materials

In addition to the predicted high specific capacity of g-GeC monolayer established in the previous section, cycling performance and rate capability of the anode material are crucial for practical application. In the case of Ge based anode material, large volume expansion during the charge/discharge process leads to poor cycling-performance and capacity loss [28,29]. However, in the case of 2D materials including graphene and germanene such a volume expansion is insignificant [14, 71]. Table 3 presents structural parameters of graphene, germanene, and germagraphene (g-GeC) before and after the lithiation and sodiation process. It is observed that the change in the lattice parameter of g-GeC monolayer after full lithiation/sodiation process is very small; about \(-0.107\%\) and \(-0.153\%\) of lattice constant change occurs after full lithiation and sodiation process, respectively. The small change in the lattice parameter is mainly explained by the relaxation of germanium atoms. As presented in the table, the buckling parameter changes upon full lithiation/sodiation, and the germanium atoms move out of the g-GeC surface.

To further evaluate the cycling and rate performance of g-GeC monolayer as anode materials, electronic properties of g-GeC after Li/Na ion adsorption as well as the diffusion of single Li/Na atoms over g-GeC surface are studied. Fig. 5 shows the band structures along with the projected density of states (PDOS) after partial lithiation and sodiation process. It is observed that the g-GeC anode material turns into the metal with bands crossing at the fermi-level, due to the charge transfer from the Li/Na atom to the germagraphene surface. The presence of increasing density of states around the Fermi-level compared to pristine g-GeC indicates that electron is transferred from Li/Na to g-GeC surface, thus improving electronic conductivity and ensuring the highest battery efficiency.

Kinetics of the electrochemical reaction is strongly influenced by the (Li/Na)-ion’s diffusion on the g-GeC surface, which eventually determines the charge-discharge behavior as well as the cyclability of LIBs and SIBs. The (Li/Na)-ion diffusion barriers on g-GeC monolayer are calculated by considering the symmetrical pathway from the most favorable site to another through the T1-and T2-sites. Both pathways with the corresponding barrier energy are given in Fig. 6. Our results

![Fig. 4](image_url)

**Fig. 4.** (a) Effect of Li/Na concentration on the adsorption energies with atoms adsorbed on both sides of the g-GeC monolayer, (b) Li/Na Open circuit voltage in (V) as a function of Li/Na concentration. Both sides of H-sites can be filled without the formation of metallic clusters.

![Fig. 5](image_url)

**Table 3**

| Material     | a (Å)  | b (Å)  | Bond Angle | \(\theta\) (Å) |
|--------------|--------|--------|------------|---------------|
| graphene     | 4.932  | 1.20   |            | 0.0           |
| Ge (germanene)| 8.036  | 1.12   | 22.9°      | 0.69          |
| g-GeC        | 6.53   | 1.20   |            | 0.0           |
| Li2GeC       | 6.537  | 104.85 |            | 0.84          |
| Na2GeC       | 6.54   | 110.15 |            | 0.66          |
show that the Li and Na-ion diffusion barrier is 0.26 eV and 0.06 eV, respectively, for pathway I, whereas 0.59 eV and 0.10 eV, respectively, for pathway II. This indicates that the (Li/Na)-ion diffusion through pathway I is faster than that in pathway II. Interestingly, our calculated barrier energy is much lower than that in similar 2D anode materials such as 2D topological semi-metal Body-Centered Orthorhombic C16 monolayer with a barrier of 0.53 eV \[72\], 2D germanene with a barrier of 2.19 eV \[14\], 2D VS2 (1H/1T phase) monolayer with a barrier of 0.62 eV \[73\], 2D h-BAs monolayer with a barrier of 0.52 and 0.24 eV, respectively, for Li- and Na-ion \[67\].

Another essential factor to evaluate the Li/Na-rate performance of germagraphene consists of the dilute Li/Na-vacancy diffusion upon the fully lithiated/sodiated configurations of g-GeC monolayer, as mentioned above both Li- and Na-atoms occupy the hollow-site after a full Li/Na concentrations. Fig. 7a despite the barrier energy of Li/Na-vacancy diffusion on the surface of Li2GeC and Na2GeC systems with a schematic illustration of the dilute Li/Na-vacancy diffusion pathway considered in our study based on the symmetry of the structure. It is obtained that the Li/Na-vacancy on Li8GeC4 and Na8GeC4 after full optimization is energetically more stable and favorable by staying in the hollow site. It is clear that the energy barrier in the case of Li-vacancy with about 0.361 eV is higher compared to the Na-vacancy 0.176 eV, and the dilute Li/Na-vacancy diffusion considered is sufficient to perform a complete connection of the 2D diffusion network on Li8GeC4 and Na8GeC4 surfaces. Hence, based on the aforementioned analysis, one can conclude that the diffusion of Na-vacancy on fully sodiated configurations of g-GeC is more rapid as predicted in the of the dilute Li/Na-ion diffusion pathways.

Moreover, we have also investigated the (Li/Na)-ion diffusion barriers inside the bi-layer of germagraphene g-GeC. The diffusion pathway with relative energy is shown in Fig. 7b. The relative energy profile is evaluated to be 0.52 eV and 0.17 eV for Li- and Na-ion, respectively.

3.5. Charge density difference in germagraphene (g-GeC)

The above-mentioned discussions unveil the capability of the g-GeC as a promising anode material for (Li/Na)-ion batteries. The (Li/Na) interaction with the monolayer can be further evaluated by considering the charge density difference. Charge density distribution of germagraphene and charge density difference of Li@GeC and Na@GeC are shown in Fig. 8. Bader charges of respective atoms are given in Table 4, where the positive/negative values represent the charge loss and charge gain, respectively. The charge density distribution of pristine g-GeC monolayer in Fig. 8a depicts charge transfer from Ge-atoms to C-atoms.

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Fig. 5. Band structures and projected density of states (PDOS) of a single (Li/Na)-atom adsorbed on g-GeC monolayer. The Fermi-level fixed at zero.

Fig. 6. The barrier energy in the diffusion of single Li- and Na-ion through two distinct paths (I & II).
Charge loss around Ge atom and charge gain around C atom are represented in Fig. 8 by sky-blue and yellow color lobes, respectively.

The charge density difference of single (Li/Na) atoms adsorbed on the germagraphene surface is presented in Fig. 8b and c. It is observed that the charge density difference for Na-case is slightly different than in the Li-case, which is associated with different electronegativity of Na (0.93) and Li (0.98) atom. From the Bader charges analysis, it is observed for the g-GeC monolayer that approximately 3.88 |e| charge is transferred through the Germanium to the Carbon atoms.

4. Conclusion

This work involved Density functional theory calculations to assess the applicability of germanium carbide monolayer as a promising negative electrode material for Li and Na-ion batteries. We find that germagraphene combines the advantages of the high Li/Na-ion storage capacity of Ge materials and structural stability of graphitic-carbon materials upon Li/Na-ion intercalation. Due to the charge redistribution in a germagraphene monolayer, Li/Na-ion adsorption on g-GeC is much stronger than that of pristine graphene material. As a result, much more Li/Na-ion can be stored in germagraphene than in graphene before the intercalation potential is decreased to 0 V. Metallic nature of Li/Na-adsorbed germagraphene ensures good electronic conductivity, while the low Li/Na-ion energy barriers of Li/Na-ion migration along the 2D diffusion network enable good ionic conductivity with negligible volume expansion. All these features together indicate that good rate performance of germagraphene as an anode can be achieved. Overall, our theoretical work affirms the feasibility of germagraphene, g-GeC, which combines the chemistry of germanene (Ge) and graphene (C), as a new class of promising anode materials for LIBs and NIBs.

CRediT authorship contribution statement

Nabil Khossossi: Conceptualization, Data curation, Formal analysis, Methodology, Validation, Visualization, Writing - review & editing.
Amitava Banerjee: Data curation, Visualization, Formal analysis,
Writing - review & editing. Ismail Essaoudi: Writing - review & editing. Abd elmajid Ainame: Writing - review & editing. Puru Jena: Writing - review & editing. Rajeev Ahuja: Supervision, Funding acquisition, Software, Project administration, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Appendix A. Supplementary data

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