



Two-dimensional sheet of germanium selenide as an anode material for sodium and potassium ion batteries: First-principles simulation study



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ABSTRACT

Recently, two-dimensional layered materials have come forth as encouraging candidates for advanced electronic and optoelectronic applications. Anode materials with high energy-density and diffusion rate are fundamental features for the development of non-lithium ion batteries. Based on the density functional theory calculations, we propose a two-dimensional (2D) sheet of germanium selenide (GeSe) as a promising anode material for a sodium (Na) or potassium (K) ion battery. The phonon dispersion and formation energy verify the dynamic and thermal stability of the GeSe sheet. A substantial charge transfer from the alkali metal atoms to the GeSe sheet enhances the electrical conductivity of GeSe, favorable for an anode material. The Na or K diffusion on the GeSe sheet has a low energy barrier of 0.10 eV, giving a rapid charge/discharge rate without metal clustering. The GeSe sheet has a high theoretical capacity for both Na (707 mA h g⁻¹) and K (530 mA h g⁻¹) ion batteries. The GeSe sheet also gives a low and stable electrode potential comparable to that of a commercial anode material.

1. Introduction

The high cost of lithium (Li) limits the applications of lithium-ion batteries (LIBs) for large-scale energy systems, such as smart grids, stationary power stations, and fully electric vehicles [1]. Consequently, sodium (Na) and potassium (K) ion batteries (NIBs and KIBs) have attracted considerable interest because of the higher abundances of Na and K and the similar storage mechanisms of NIBs and KIBs to those of LIBs [2–7]. A successful commercialization of NIB or KIB is limited by, among others, the lack of a suitable anode material [8,9] with a rapid charge/discharge rate, a high storage capacity, and a good capacity retention.

In this regard, two-dimensional (2D) materials, having high surface areas and superior electronic properties [10], are considered as anode materials of LIBs, NIBs, and KIBs [11–16]. For example, a 2D black phosphorus, phosphorene, gives a high storage capacity in NIB [17–19], but it is thermally unstable and highly reactive towards O₂ and H₂O [20–22]. Graphene contact or hexagonal boron nitride (h-BN) encapsulation of phosphorene [23,24] were proposed as strategies to prevent the oxidative degradation. In contrast, 2D materials of group-IV monochalcogenides MX (M = Si, Ge or Sn; X = S or Se) are known for their stability, abundance, and environmental friendliness [25–29]. By comprehensive first-principle calculations Zhou et al. showed that, compared to phosphorene, the monolayers of group-IV

monochalcogenides have enhanced oxidation resistivities and thermodynamic stabilities under ambient conditions [29]. A theoretical study showed a 2D GeS sample has nice features of the theoretical capacity and charging rate for NIB application [21]. Among monochalcogenides, the 2D sheet of GeSe has a direct band gap [26]. Multi-layered sheets of GeSe are recently applied to photovoltaic and photodetector applications [30–32]. An anode material made from GeSe nanocrystals shows an excellent capacity retention for LIB [33]. Kim et al. reported that a comb-shaped GeSe has high rate capability (331 mA h g⁻¹ at 20 C) and remarkable cyclability (650 mA h g⁻¹ even after 1000 cycles) when used in a LIB [34]. In addition, first-principle study showed that a 2D sheet of GeSe can be a good candidate for LIBs [35].

However, currently, the applicability of a 2D GeSe sheet for a NIB or KIB is unknown. Herein, the density functional theory (DFT) simulations are performed to provide a comprehensive understanding on the prospective application of a single-layered GeSe sheet for NIB or KIB. The thermal and dynamic stabilities of the GeSe sheet and the practicality of its isolation from the bulk GeSe are confirmed. The Na or K diffusion on the GeSe sheet has a low energy barrier of 0.1 eV. Moreover, the 2D GeSe sheet gives high theoretical capacities and low and stable voltages for NIB and KIB. All these results indicate that a GeSe sheet is a prospective anode material which gives a high-power density and a rapid charge/discharge rate.

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2. Computational details

All the DFT calculations are performed using the Vienna ab initio simulation package (VASP) [36,37]. The electron-ion interactions are considered using the projector-augmented wave method [38]. We treat the exchange correlation within the generalized gradient approximation in the form of the Perdew–Burke–Ernzerhof [39] functional. We use an energy cutoff of 500 eV in the plane-wave expansion of a valence electron wave function. The van der Waals interactions are included using the semiempirical correction scheme of Grimme (DFT + D2) [40] which successfully describes the binding energy and diffusion of lithium on graphite [41]. To examine the adsorption and diffusion of metal atoms, we model the 2D GeSe sheet as a 3×3 slab, repeated periodically along the X and Y directions. A 20 Å-thick vacuum space is introduced along the Z-direction to avoid the spurious interactions between the GeSe sheet and its periodic images. We optimize both the lattice constants and atomic coordinates using the conjugate gradient scheme without imposing any symmetry restrictions. A geometry optimization is taken to be converged if the change in energy is $< 10^{-5}$ eV and the maximum force on each atom is < 0.02 eV Å⁻¹.

We check the dynamic stability of the GeSe sheet by calculating its phonon dispersion spectra using the Phonopy code [42]. The Brillouin zones of the 2D and bulk GeSe are sampled using $4 \times 4 \times 1$ and $4 \times 3 \times 4$ Monkhorst-Pack [43] k-point grids, respectively. We use a denser mesh of $12 \times 12 \times 1$ to calculate the DOS and band structure of the GeSe sheet. We employ the Bader charge analysis [44–46] to determine the amount of charge transfer between metal and GeSe. We study the diffusion of alkali metal atom by constructing the minimum energy path based on the climbing image nudged elastic band (CI-NEB) method implemented in the VASP transition state tools [47,48]. Nine images are used, including the initial and final configurations in the CI-NEB calculation. The zero-point energy (ZPE) and quantum tunneling effects on the present ionic diffusion are expected to be small, as found for Li diffusions on 2D SiS and SiSe [49] and Na diffusions in hexagonal boron nitride/black phosphorene heterostructure [50].

3. Results and discussions

3.1. Structure of GeSe nanosheet

Our calculation gives the lattice parameters of the bulk GeSe as $a = 3.87$ Å, $b = 4.53$ Å, and $c = 11.142$ Å, which are consistent with the previous theoretical studies using PW91 and PBE functional

[25,27]. The maximum deviations are within 3%. The 2D GeSe sheet shows a puckered layer structure [51] (as shown in Fig. 1). The calculated lattice parameters are $a = 3.94$ Å and $b = 4.42$ Å. The lattice parameters agree with previous computation using PBE functional (deviation $< 1\%$) [26]. The 2D GeSe have two distinct Ge–Se bond lengths, $l_1 = 2.61$ Å and $l_2 = 2.54$ Å (Fig. 1a).

The thickness of the GeSe d ($= 2.52$ Å) is greater than that of phosphorene ($= 2.10$ Å) (Fig. 1a). We estimate the thermodynamic stability of the GeSe sheet by calculating the formation energy E_f defined as

$$E_f = E_{\text{GeSe}} - E_{\text{Ge}} - E_{\text{Se}} \quad (1)$$

where E_{GeSe} is the energy of the GeSe sheet and E_{Ge} and E_{Se} are the energies of Ge and Se atoms in the bulk, respectively. E_f is found to be -0.25 eV per unit cell, confirming that the GeSe sheet is thermodynamically stable (ignoring the entropic contribution which is negligible at room temperature) [52,53].

We assess the dynamic stability of the GeSe sheet by examining the phonon dispersion calculated using the density functional perturbation theory [54]. The phonon spectra do not exhibit any imaginary frequency (Fig. S1), proving the vibrational stability of the GeSe sheet. Twelve modes of vibrations are present: three acoustic (lower curves) and nine optical modes (upper curves). The optical and acoustic branches are well separated, as found for other 2D materials, such as graphene [55], phosphorene [56], and stanene [57]. We evaluate the exfoliation energy of the GeSe sheet, E_{exf} , as

$$E_{\text{exf}} = \left(\frac{E_{\text{bulk}}}{N} - E_{\text{mono}} \right) \quad (2)$$

where E_{bulk} and E_{mono} are the energies of the bulk GeSe made from N ($= 2$) layers per unit cell and the GeSe sheet, respectively. Compared to the traditional few-layer slab model, the present method gives exfoliation energies with less computation time and reasonable accuracy [15,58,59]. We find $E_{\text{exf}} = 0.14$ eV per unit cell, comparable to those of the experimentally synthesized graphene (0.21 eV), boron nitride (0.28 eV) [59], MoN₂ (0.17 eV) [15], and MoS₂ (0.16 eV) [15,58]. Therefore, a common method such as mechanical exfoliation [60,61] and liquid exfoliation [62,63] can be used to grow the GeSe sheet.

3.2. Adsorption of alkali metal atoms on GeSe nanosheet

We examine how strongly the GeSe sheet binds the alkali metal atoms. A weak binding of metal can give an undesirable metal

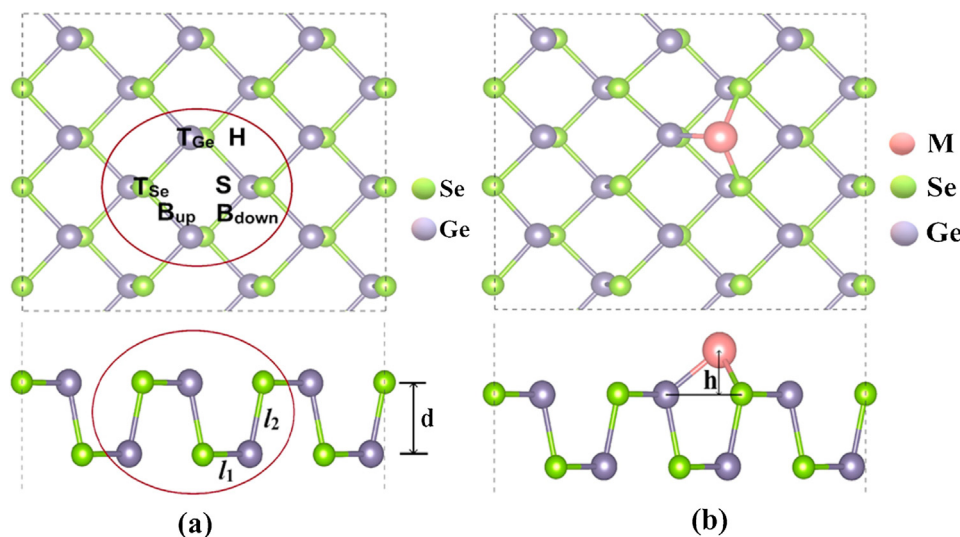


Fig. 1. (a) Adsorption sites on the 2D GeSe sheet labelled with different letters (H, S, T, and B). The circles denote the unit cells. (b) An alkali metal atom (Li in this case) adsorbed at site H which gives the strongest metal adsorption. In each panel, the top and side views are shown together.

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