Ab initio prediction and characterization of phosphorene-like SiS and SiSe as anode materials for sodium-ion batteries

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ABSTRACT

In this work, a density functional theory (DFT) based first-principles study is carried out to investigate the potential of phosphorene-like SiS and SiSe monolayers as anode materials for sodium-ion (Na-ion) batteries. Results show that both SiS and SiSe have large adsorption energies towards single Na atom of \(-0.94\) and \(-0.43\) eV, owing to the charge transfers from Na to SiS or SiSe. In addition, it is found that the highest Na concentration for both SiS and SiSe is \(x = 1\) with the chemical formulas of NaSiS and NaSiSe, corresponding to the high theoretical specific capacities for Na storages of 445.6 and 250.4 mAh g\(^{-1}\), respectively. Moreover, Na diffusions are very fast and show strong directional behaviors on SiS and SiSe monolayers, with the energy barriers of only 0.135 and 0.158 eV, lower than those of conventional anode materials for Na-ion batteries such as Na\(_2\)Ti\(_3\)O\(_7\) (0.19 eV) and Na\(_3\)Sb (0.21 eV). Finally, although SiS and SiSe show semiconducting behaviors, they transform to metallic states after adsorbing Na atoms, indicating enhanced electrical conductivity during battery cycling. Given these advantages, it is expected that both SiS and SiSe monolayers are promising anode materials for Na-ion batteries, and in principle, other Na-based batteries as well.

1. Introduction

With the widely applications ranging from portable electronic devices to electric vehicles, lithium-based batteries are regarded as one of the most promising energy storage technologies that power the world [1–17]. However, the limited natural resource of lithium hinders their further application in large-scale energy storage systems. In this regard, over the past decades, great efforts have been made to explore the substitute battery systems which are cheap and leave little burden on the environment, including sodium-ion (Na-ion) batteries [18–23], sodium-sulfur (Na-S) batteries [24,25] and redox flow batteries [26–29]. Among the state-of-art battery systems, Na-ion batteries attract much attention due to their low cost and comparable battery performances with Li-ion batteries, attributed to the natural abundance of sodium and chemical similarity among alkali metals. Even though, the development of Na-ion batteries is limited by several critical issues, and the absence of an appropriate anode material is one of the most severe [19,30–33]. Due to the larger size (1.02 Å vs. 0.76 Å for Li) and higher ionization potential of Na than Li atom, many potential anode materials for Li-ion batteries are not suitable to be used in Na-ion batteries. For example, graphite, the commercialized anode material for Li-ion batteries, can only form an eighth-stage intercalation compound NaC\(_{64}\) with Na because of the highly inefficient Na interaction, corresponding to a very low capacity for Na-ion batteries [34,35]. Other intensively investigated anode materials such as Na\(_2\)Ti\(_3\)O\(_7\), NiCo\(_2\)O\(_4\), FeS\(_2\), Sn/C and Sb/C also suffer from critical issues including severe capacity decay, slow kinetics and significant volume change [21,36–41]. Therefore, seeking for appropriate anode materials is vitally important to the development of Na-ion batteries.

In this regard, two-dimensional (2D) materials arouse great research interests and are considered to be the promising candidates to form anode in Na-ion batteries, due to their advantages of large surface-to-volume ratio and unique electronic property. Until now, a variety of 2D materials have been predicted to be the potential anode materials with enhanced theoretical specific capacities and ion diffusivities for Na-ion batteries. For example, phosphorene was found to have a high specific capacity of 865 and 433 mAh g\(^{-1}\) for double- and single-side Na adsorption, as well as a fast Na diffusivity with a small energy barrier of 0.04 eV [42]. Ti\(_3\)C\(_2\) MXene was discovered to be a potential anode material due to a high specific capacity of 351.8 mAh g\(^{-1}\) and a low Na diffusion barrier of 0.096 eV [43]; Mo\(_x\)C was also predicted to have a specific capacity of 263 mAh g\(^{-1}\) and a Na diffusion barrier as low as 19 meV [44].

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Although some progresses have been made, the efforts of designing new 2D materials with high performance for Na-ion batteries are never diminished. One effective approach to design new materials is “atomic transmutation”, which replaces one type of element with its neighboring two elements in the periodic table but keeps the total number of valence electrons constant \([45]\). With this strategy, recently, a IV-VI group material SiS was predicted by changing two P atoms in group V phosphorene into one Si atom in group IV and one S atom in group VI, including four potential structures of \(\alpha\)-SiS, \(\beta\)-SiS, Pma2-SiS and silicene sulfide \([45,46]\). Once predicted, the SiS monolayer attracts much attention due to its unique properties, such as good mechanical and chemical stability, high nanoelectronic mobility, strong anisotropy behavior for optical sensors, and potential application for photovoltaic \([45]\). In addition, inspired by the successful synthesis of 2D ordered, stoichiometric and solid-state graphene oxide with C:O ratio of 1:1 by Mattsson et al. \([47]\), the SiS monolayer might be synthesized starting from silicene at low temperature in the future \([45]\). To better understand the electrochemical performance of 2D SiS, Jiang et al. \([48]\) investigated the potential of \(\alpha\)-SiS, \(\beta\)-SiS, Pma2-SiS and silicene sulfide as the anode materials for Li-based batteries. They found that \(\alpha\)-SiS showed the most promise due to its high specific capacity of 446 mAh g\(^{-1}\), low lithium diffusion barrier of 0.17 eV and enhanced electrical conductivity after lithiation. In the meantime, Karmakar et al. \([49]\) compared the feasibility of phosphorene-like, corresponding to the structure of \(\alpha\)-SiS, group IV monochalcogenides (SiS, SiSe, GeS, GeSe, SnS and SnSe) monolayers to act as anode materials in Li-ion batteries. Their results showed that SiS and SiSe monolayers had the best predicted performance among samples studied. Inspired by these works, an interesting question arises naturally and promptly: can SiS and SiSe monolayers be promising anode materials for Na-ion batteries? However, until now, the investigation on the potential application of SiS and SiSe monolayers in Na-ion batteries is still missing. To answer this question, a detailed study of the Na adsorption and diffusion on SiS and SiSe monolayers is indispensable.

In this work, first-principles calculations were carried out to investigate the potential of free-standing SiS and SiSe monolayers as the anode materials in Na-ion batteries. The structures of SiS and SiSe monolayers were firstly optimized and compared with previous works. Secondly, the adsorption energies of Na atom on high-symmetry sites were calculated. Thirdly, the effects of Na concentrations on adsorption energies were clarified and the theoretical specific capacities of SiS and SiSe monolayers as anode materials in Na-ion batteries were obtained. Then, the Na diffusion barriers in representative directions of SiS and SiSe monolayers were calculated. Finally, to analyze the electronic properties, the electron density states (DOS) of Na-adsorbed structures were investigated. Although the SiS and SiSe monolayers have not been successfully synthesized, the purpose of our work is to find the potential applications of these new materials, which gives an in-depth understanding into 2D materials and inspires the experimental community to make this prediction come true.

2. Computational methods

All density functional theory (DFT) based first-principles calculations were performed by using ABINIT \([50,51]\) code adopting generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) type \([52]\). The electron-ion interactions were considered by Projector-augmented-wave (PAW) potentials \([53]\). The energy cutoff was set to 24 Ha (1 Ha = 27.211 eV) to ensure a satisfied convergence for wave-basis expansion. To avoid image-image interaction, a vacuum layer of 20 Å was added in the slab models. The spacing between K-point grids was all set to be less than 0.05 Å\(^{-1}\). The force convergence criteria for self-consistent-field cycles and structural relaxation were set to 4.0 \(\times\) \(10^{-5}\) and 6 \(\times\) \(10^{-5}\) Ha Bohr\(^{-1}\) (1 Bohr = 0.529 Å), respectively.

The adsorption energy of Na atoms on SiS or SiSe monolayers was calculated on a 3 \(\times\) 4 supercell by

\[
E_{\text{adh}} = \frac{(E_{\text{SiS,\text{SiSe}+Na}} - n \cdot \mu_{\text{Na}} - E_{\text{M}})/n.}
\]

where \(E_{\text{SiS,\text{SiSe}+Na}}\) and \(E_{\text{M}}\) are the DFT energies of SiS or SiSe monolayer with and without Na atoms; \(\mu_{\text{Na}}\) is the chemical potential of Na, getting from the body centered cubic (BCC) bulk structures of Na; \(n\) is the number of Na atoms. The negative values of adsorption energy stand for that the adsorbed system is more stable than the two separated systems.

When the volume and entropy effects during Na loading process are neglected, the average voltage in the concentration range of \(x_1 \times x_2 \times x_3\) can be obtained by \([54-56]\):

\[
V \approx \frac{E_{\text{Na}} - E_{\text{SiS,\text{SiSe}+Na}} - E_{\text{SiS,\text{SiSe}}} + (x_2 - x_1)E_{\text{Na}}}{(x_2 - x_1)e},
\]

where \(E_{\text{Na}}\) and \(E_{\text{SiS,\text{SiSe}}}, E_{\text{SiS,\text{SiSe}+Na}}\) and \(E_{\text{M}}\) are the total energies of Na, SiS/SiSe, Na_SiS/SiSe, Na_{iSiS/SiSe} and Na atom, respectively.

The temperature-dependent molecular transition rate \((D)\) was investigated by Arrhenius equation

\[
D \sim \exp \left(\frac{-E_a}{k_B T}\right)
\]

where \(E_a\), \(k_B\) and \(T\) are diffusion barrier, Boltzmann’s constant and temperature, respectively. The simplified string method \([57,58]\) was used to calculate the Na diffusion barriers.

3. Results and discussion

The schematic structures (top and side views) of free-standing SiS and SiSe monolayers are shown in Fig. 1a and b. It is found that both SiS and SiSe monolayers have puckered surfaces with each atom bonded to three different kind of atoms, two of which in same layer, and one of which in different layer. The calculated lattice parameters for SiS monolayer are \(a = 4.60\) Å and \(b = 3.27\) Å, while those for SiSe monolayer are \(a = 5.00\) Å and \(b = 3.54\) Å, consistently with previous theoretical results \([46,49]\). In addition, the lattice parameters of SiS monolayer are smaller than those of phosphorene \((a = 4.62\) Å and \(b = 3.30\) Å \([59]\), but those of SiSe monolayer are larger than phosphorene. The calculated Si-S bond lengths in same and different layers for SiS monolayer are 2.28 and 2.34 Å, while those of Si-Se bond lengths for SiSe monolayer are 2.46 and 2.49 Å.

As the promising anode materials for Na-ion batteries, it is a necessary prerequisite for both SiS and SiSe monolayers to have strong adsorption energies to Na atom. Therefore, we first calculate the adsorption energies of SiS and SiSe monolayers towards single Na atoms. Considering the high symmetry of SiS and SiSe monolayers, as shown in Fig. 1c, three representative adsorption sites are chosen: (1) \(H_1\) site: above the hollow of \(\text{Si}_3\text{S}_3/\text{Si}_3\text{Se}_3\) hexagon, bonded to two Si atoms and one S/Se atom; (2) \(H_2\) site: above the hollow of \(\text{Si}_3\text{S}_3/\text{Si}_3\text{Se}_3\) hexagon, bonded to one Si atom and two S/Se atoms; (3) \(B\) site: above the midpoints of the bottom SiS/Si-Se bond. The calculated results are summarized in Table 1. It is found that \(H_1\) site shows the largest Na adsorption energy for both SiS and SiSe monolayers, indicating Na atoms prefer to locate at \(H_1\) site during loading. In addition, \(B\) site is not the stable adsorption site for Na atoms, at which Na atom moves to \(H_2\) site during structural optimization with no energy barrier. In the case of SiS monolayer, the Na adsorption energies on \(H_1\) and \(H_2\) sites are \(-0.94\) and \(-0.90\) eV, respectively. At the most stable \(H_1\) site, the optimized Si-Na and S-Na bond lengths are 3.00 and 2.79 Å. In
the case of SiSe monolayer, the Na adsorption energies on H1 and H2 sites are \(0.43\) and \(0.39\) eV, with the optimized Si-Na and Se-Na bond lengths are 3.00 and 2.89 Å at the most stable H1 site.

To have a mechanistic understanding on the charge transfer process of Na atom adsorbed on H1 site of SiS and SiSe monolayers, the charge difference plot is used and the charge difference is calculated by

\[
\Delta \rho = \rho_{\text{Na-SiS/SiSe}} - \rho_{\text{Na}} - \rho_{\text{SiS/SiSe}}.
\]

where \(\rho_{\text{Na-SiS/SiSe}}\), \(\rho_{\text{Na}}\) and \(\rho_{\text{SiS/SiSe}}\) are the charge densities of Na-adsorbed systems, isolated Na atom and SiS/SiSe monolayer, respectively. The charge difference plots of Na adsorbed on SiS and SiSe monolayers are shown in Fig. 2a and b, with yellow and blue areas representing for electron gain and loss. Due to the electronegativities of Si, Se and S are larger than that of Na, an obvious net loss of charges around Na atom and a net gain of charges above SiS/SiSe monolayer are found, indicating a significant charge transfer from Na to the substrate.

Furthermore, the anode materials for Na-ion batteries should have a high Na storage capacity. In this regard, the effect of Na concentrations on the adsorption energy changes is investigated and the highest theoretical specific capacity is obtained accordingly. Here, we consider a series of higher configurations with stoichiometry of Na\(_{0.0833}\)SiS/Na\(_{0.0833}\)SiSe, Na\(_{0.1111}\)SiS/Na\(_{0.1111}\)SiSe, Na\(_{0.1667}\)SiS/Na\(_{0.1667}\)SiSe, Na\(_{0.25}\)SiS/Na\(_{0.25}\)SiSe, Na\(_{0.5}\)SiS/Na\(_{0.5}\)SiSe and NaSiS/NaSiSe, as shown in Fig. 3a-f, by adding two Na atoms to both sides of a 3 \times 4, 3 \times 3, 2 \times 3, 2 \times 2, 1 \times 2 and 1 \times 1 supercell, respectively. The corresponding adsorption energy changes and lattice constant changes as the function of Na concentrations in Na\(_x\)SiS and Na\(_x\)SiSe are shown in Fig. 4a-d. It is seen that the adsorption energy decreases as the Na concentrations increase for both SiS and SiSe monolayers. Generally, it is known that there are two kinds of competitive effects existing as the increasing concentration: one is the repulsion force between neighboring atoms, which decreases the adsorption energy; the other is the induced structural changes of substrates, which increases the adsorption energy. Here, for both SiS and SiSe monolayers, it is obvious that the increasing repulsion force is the dominant one. In the case of SiS monolayer, the initial adsorption energy is \(-0.62\) eV at the Na concentration of \(x = 0.0833\). Then, when the concentration increases to \(x = 0.1111\), the adsorption energy decreases dramatically to \(-0.529\) eV. With the concentration continuously increases from 0.1667 to 0.25, and then to 0.5, the adsorption energy decreases from \(-0.430\) eV to

Table 1

<table>
<thead>
<tr>
<th>Site</th>
<th>SiS site</th>
<th>SiSe site</th>
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<tr>
<td>H1 site</td>
<td>(-0.94) eV</td>
<td>(-0.90) eV</td>
</tr>
<tr>
<td>H2 site</td>
<td>(-0.43) eV</td>
<td>(-0.39) eV</td>
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Fig. 1. (Color online) The schematic structures of (a) top and (b) side views of free-standing SiS and SiSe monolayers. (c) Considered representative adsorption sites on SiS and SiSe surfaces.

Fig. 2. (Color Online) The charge difference plots of Na atom adsorbed on (a) SiS and (b) SiSe. The yellow and blue areas represent for electron gain and loss.
−0.332 eV, and then to −0.214 eV. The highest concentration is $x = 1$, at which the surfaces of both sides of SiS monolayer are fully covered by Na atoms, and the corresponding adsorption energy is −0.097 eV. In the case of SiSe monolayer, initially, the adsorption energy is −0.370 eV at the Na concentration of $x = 0.0833$. As the concentration increases to $x = 0.1111$, the adsorption energy
decreases to $-0.341$ eV. Then, when the concentration continuously increases from 0.1667 to 0.25, and then to 0.5, the adsorption energy decreases from $-0.303$ to $-0.236$ eV, and then to $-0.175$ eV. Finally, the Na concentration would arrive the highest value of $x = 1$, and the corresponding adsorption energy is calculated to be $-0.108$ eV. Compared the results in SiS monolayer with those in SiSe monolayer, it is also interesting to find that although the Na adsorption energy on SiS monolayer is larger than that on SiSe monolayer at low Na concentration, it decreases much faster than that on SiSe monolayer as the Na concentration increases. This phenomenon can be attributed to the larger lattice parameters of SiSe than SiS, which is consistent with the larger atomic radius of Se than S, leading to the less enhanced repulsion force in SiSe monolayer than in SiS monolayer as the Na concentration increases.

The average voltages of SiS and SiSe monolayers for Na storage are calculated to be 0.097 and 0.108 V, respectively. For one thing, the positive values ensure the successful loading of Na atoms, which is the basic requirement for the electrode materials in Na-ion batteries. For another thing, the average open circuit voltages for Na storage are all less than 0.2 V, indicating good structural stabilities when used as anode materials.

Based on the calculated results, the theoretical specific capacities ($C$) of Na atoms on SiS and SiSe monolayers are expressed by

$$C = \frac{1}{M_{\text{SiS/SiSe}}} (x_{\text{max}} \times F \times 10^3),$$

where $x_{\text{max}}$ is the highest concentration of Na on SiS and SiSe monolayers; $F$ is the Faraday constant of 26.810 Ah mol$^{-1}$; and $M_{\text{SiS/SiSe}}$ is the atomic mass of SiS or SiSe monolayer. From the adsorption energy changes in Fig. 4a and b, it is found that the highest concentrations of Na on both SiS and SiSe monolayers are all $x = 1$, corresponding to the chemical formulas of NaSiS and NaSiSe. Based on Eq. (5), the theoretical specific capacities of SiS and SiSe monolayers for Na storages are calculated to be 445.6 and 250.4 mAh g$^{-1}$, respectively. In comparison with other anode materials for Na-ion batteries, SiSe monolayer shows larger theoretical specific capacity than MoS$_2$ (146 mAh g$^{-1}$) [60], while the theoretical specific capacity of SiS monolayer is even larger than that of Ti$_3$C$_2$ MXenes (352 mAh g$^{-1}$) [43] and phosphorene (433 mAh g$^{-1}$) [42]. Therefore, both SiS and SiSe monolayers can be the promising high specific capacity anode materials for Na-ion batteries.

In addition to the theoretical specific capacity, another fundamental criterion to evaluate whether SiS and SiSe monolayers are suitable to be used as anode materials in Na-ion batteries is the rate performance, largely depending on the mobility of Na atoms and the electrical conductivity of anode materials. Therefore, in this part, we first investigate the diffusion pathways and calculate the energy barriers of Na atom diffusing on SiS and SiSe monolayers, as shown in Fig. 5. Due to the highly symmetric structure of SiS and SiSe monolayers, three representative diffusion pathways are considered: path 1 goes through two midpoints of the bottom Si-S/Si-Se bonds, being along the zigzag direction, as shown in Fig. 5c; path 2 goes the top of S/Se atom, being along the armchair direction, as shown in Fig. 5d; path 3 goes through one midpoint of the top Si-S/Si-Se bond and one midpoint of the bottom Si-S/Si-Se bond, as shown in Fig. 5e. From our results, it is found that both SiS and SiSe monolayers show directional anisotropies for Na atom, with the diffusion barriers increasing in the sequence of path 1 < path 2 < path 3. In the case of SiS monolayer, the diffusion barriers along path 1, 2 and 3 are 0.135, 0.415 and 0.542 eV, respectively. Based on the Arrhenius equation, the Na diffusion along
path 1 is $10^4$ times faster than that along path 2, and $10^6$ times faster than that along path 3. The similar phenomenon is also observed for Na diffusion on SiS monolayer, with the energy barriers along path 1, 2 and 3 are 0.158, 0.479 and 0.528 eV. Accordingly, the Na diffusivity along path 1 is $10^6$ higher than that along path 2, and $10^8$ times higher than that along path 3. Compared with other anode materials for Na-ion batteries, both SiS and SiSe monolayers show lower diffusion barrier and higher Na diffusivity. The Na diffusion barriers on SiS and SiSe monolayers are 0.135 and 0.158 eV, respectively, lower than that on other investigated anode materials such as Ti$_2$CO$_2$ (0.18 eV) [61], Na$_2$Ti$_3$O$_7$ (0.19 eV) [36], Na$_3$Sb (0.21 eV) [62], MoS$_2$ (0.28 eV) [60] and B-doped graphene (0.16 eV) [63]. Therefore, both SiS and SiSe monolayers can facilitate the faster transport of Na atom.

Moreover, the electronic properties of anode materials also play a vitally important role on the rate performance. Thus, we further calculate the DOS of pristine SiS and SiSe monolayers. As shown in Fig. 6a, both SiS (1.40 eV) and SiSe (1.14 eV) monolayers have smaller band gaps than the conventional anode material Na$_2$Ti$_3$O$_7$ (2.75 eV) [36], indicating higher electrical conductivities. However, compared with other predicted anode materials for Na-ion batteries, such as graphene, Mo$_2$C and borophene [7,64–66], SiS and SiSe monolayers have lower electrical conductivity because of their semiconducting behaviors. In this regard, it is necessary to examine the electronic properties of SiS and SiSe monolayers with Na intercalations. The DOS of SiS and SiSe monolayers after adsorbing Na atom are shown in Fig. 6b. It is found that although pristine SiS and SiSe monolayers are semiconductors, when Na atom involved, the Fermi levels are shifted and the Na-SiS/Na-SiSe systems are changed from semiconducting to metallic states, indicating much enhanced electrical conductivity, as shown in Fig. 3b and d. This phenomenon is also observed in other potential anode materials, such as phosphorene [67], α-SiS [48] and SeS [68], attributed to the electron-donating behavior of metal atoms and electron-withdrawing behaviors of substrates. Thus, the metallic behavior ensures both SiS and SiSe anodes to have an excellent electrical conductivity for Na-ion batteries during cycling.

4. Conclusion

To conclude, a DFT based first-principles study is carried out to investigate the potential of SiS and SiSe monolayers as the anode materials for Na-ion batteries. It is found that H$_1$ site is the most stable one for Na adsorption on both SiS and SiSe monolayers, with the adsorption energy of $-0.94$ and $-0.43$ eV, respectively. From charge difference plots, it is also found an obvious net loss of charges around Na atom and a net gain of charges above SiS and SiSe monolayers, indicating a great deal of charges transfer from Na to SiS and SiSe monolayers, which is attributed to the larger electronegativities of Si, S and Se than Na. In addition, we investigate the effect of Na concentrations on adsorption energy changes and calculate the theoretical specific capacities. It is shown that the highest Na concentration for both SiS and SiSe monolayers is $x = 1$ with the chemical formulas of NaSiS and NaSiSe, corresponding to high Na storage capacities of 445.6 and 250.4 mAh g$^{-1}$ for SiS and SiSe monolayers, respectively. To evaluate the rate capability of SiS and SiSe monolayers as anode materials in Na-ion batteries, the Na diffusion barriers and the electrical conductivities of them are calculated. Results show that Na has high diffusivities on both SiS and SiSe monolayers, with the energy barriers of 0.135 and 0.158 eV, respectively. Meanwhile, Na diffusions along path 1 is more than $10^4$ times faster than that along path 2 and 3 for both SiS and SiSe monolayers, indicating strong directional anisotropies. In addition, although both SiS and SiSe monolayers show semiconducting behaviors, they transform to metallic states after Na interaction, ensuring enhanced electrical conductivities. Given these advantages, it is expected that both SiS and SiSe monolayers are promising anode materials for Na-ion batteries, and in principle, other Na-based batteries as well.

Conflict of interest

The authors declare that they have no conflict of interest.

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