Can P$_3$S and C$_3$S Monolayers be Used as Anode Materials in Metal-Ion Batteries? An Answer from First-Principles Study

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ABSTRACT

With the urgent need for efficient energy storage devices, enormous attention has been paid to researching and developing promising anode materials for metal-ion batteries. Through density functional study, we have successfully predicted the electrochemical performance of the P$_3$S and C$_3$S monolayers for the first time, which could be used in alkali metal (Li, Na, and K)-ion batteries. Our study examines the pristine monolayers' energetical, dynamical, and thermal stability. The electronic structures of the pristine nanosheets exhibit wide-gap semiconductors. After single metalation on the monolayers, the composite systems become metallic. Charge density difference (CDD) analysis indicates that charge transfer occurs from the alkali metal atoms to the P$_3$S and C$_3$S monolayers, and Bader charge analysis quantifies the amount of charge transfer. We have analyzed how readily a single adatom diffuses within the 2D structures. One example is the diffusion of K on C$_3$S, which has a low barrier value of 0.06 eV and seems practically barrierless. Furthermore, our predicted composite systems report considerable theoretical storage capacity (C); for example, hexalayer K-adsorbed C$_3$S shows a storage capacity of 1182.79 mA h g$^{-1}$. The estimated open-circuit voltage (OCV) values imply that the C$_3$S monolayer is promising anode material for Li-, Na-, and K-ion batteries, while the P$_3$S monolayer is suitable as cathode material for Li-, Na-, and K-ion batteries.

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INTRODUCTION

With the expansion of the global population, the crisis of energy and environmental issues have evolved one after another. The continuous depletion of non-renewable energy sources like natural gas, petroleum, coal, etc., has affected the global climate and threatened human health and lives. However, one may overcome this situation using renewable energy sources such as biomass, solar, wind, tidal, and geothermal energy. Thus, there is a global need for environmentally benign alternative energy sources for power generation systems and power grids on a larger scale to meet the energy demands and the environmental aspects. In this scenario, electrochemical energy storage (EES) systems play a vital role in improving the grid's reliability and supply of energy. In the last few decades, the scientific communities have witnessed the growth of energy storage devices like rechargeable batteries (secondary storage systems), supercapacitors, etc. Designing a secondary storage system has become challenging due to the diverse market need. Thus, after various modifications of secondary storage systems, scientific researchers have developed sustainably by introducing metal-ion batteries (MIBs). The MIBs are promising candidates for the EES systems due to their high charge density, fast charging-discharging rate, outstanding efficiency, and structural rigidity. Recently, MIBs have significantly impacted the advancement of electronic devices according to consumer needs. This research area focuses on univalent (alkali metals: Li, Na, and K) and multivalent (Mg, Ca, Zn, and Al) MIBs. In this energy crisis, the alkali metal-based MIB research is fascinating with contemporary interests.

Two-dimensional (2D) materials have enriched various fields of science and technology with widespread potential applications, viz., energy storage devices, optoelectronic devices, catalysis, etc. The 2D structures are generally layered materials, in which the in-plane atoms are strongly bonded, whereas the adjacent layers bind via weak van der Waals (vdW) force of attraction. These 2D layered materials have some superiority over their bulk counterpart in some aspects, such as (i) due to the quantum confinement effect along the out-of-plane direction, the bandgaps of the 2D materials depend on the number of layers, which contribute significantly to the designing of optoelectronic devices, (ii) the surface of the materials is free from dangling bonds due to the presence of interlayer vdW force that makes the materials more stable compared to their bulk structures, (iii) this interlayer vdW force also facilitates to overcome for modeling of heterostructures of the 2D materials, (iv) high surface-to-volume ratio of the materials offer more active sites, etc. These properties make them excellent materials for electrochemical performance. Many 2D materials have been developed, characterized, and utilized for various potential applications to date. However, the scientific revolution of 2D materials started after graphene's successful peeling in 2004. Later, graphene was synthesized by numerous research groups and utilized for various potential applications. Its energy storage application is noteworthy among the other 2D materials. Many theoretical and experimental studies have established graphene-based energy storage systems. The theoretical storage capacity of graphene in Li-ion batteries is found to be 744 mA h g⁻¹. But the practical result significantly differs from the theoretical value due to the aggregation during the charging-discharging process. Thus, to enhance the energy storage performance of graphene, a few promising modification strategies have been employed, viz., controllable surface functionalization, prelithiation, and composite materials. As a result, graphene heterostructure was modeled with other 2D materials like MXene, BN, and black phosphorus to enhance the storage capacity.
In recent times, phosphorene has triggered the two-dimensional research domain for its potential applications. It can be synthesized by liquid or mechanical exfoliation of bulk black phosphorous (BP). It exhibits quadrangular pyramidal geometry where each P atom is covalently connected to the nearest neighboring three P atoms at 2.18 Å with one lone pair to form a puckered honeycomb structure. Two of the P atoms are in the plane of the layer by maintaining a 99° angle, and the third remains between the layers with an average bond angle of 102°. This unique geometry originates high anisotropic electrical and thermal mobility and optical response. Phosphorene is a direct band gap semiconductor. The material's band gap can be altered from 0.3 eV to 1.88 eV by modifying the bulk into a monolayer. Phosphorene has shown its substantial ability as electrode material in various metal-ion batteries. Xue et al. theoretically established that phosphorene monolayer can behave as potential anode material for lithium-ion batteries (LIBs) with a theoretical specific capacity of 432.79 mA h g⁻¹ and moderate Li-ion diffusion barrier of 0.76 eV. In another study, Zhang et al. showed a strong directional anisotropy of Li-ion diffusion in phosphorene. They found the diffusion barrier of Li-ion along armchair and zigzag directions are 0.68 and 0.08 eV respectively. Wu et al. studied phosphorene as an anode material for Na-ion batteries (SIB) with a theoretical specific capacity of 865 mA h g⁻¹ and a Na-diffusion barrier of only 0.04 eV. Among the four different allotropic forms (β, γ, δ, and ζ) of phosphorene, the β-phase (blue phosphorene) can exhibit excellent anodic behavior in LIBs. The vdW heterostructure of blue phosphorene with various 2D materials like graphene, TMDs, borophene, C₃N, etc., has already emerged as promising anode materials for various alkali metal-ion batteries due to their high storage capacity, excellent mechanical stability, ultrahigh conductivity, strong adsorption, and low diffusion barrier of the metal ion. The blue phosphorene/graphene heterostructure shows ultrahigh stiffness in the 353-422 N m⁻¹, a theoretical specific capacity of 626 mA h g⁻¹, and a low Li-migration barrier 0.13 eV. Cui et al. have experimentally reported a sandwiched phosphorene/graphene hybrid structure for SIB that exhibits an ultrahigh specific capacity of 2440 mA h g⁻¹ and 83% capacity retention after 100 cycles. The blue phosphorene/MS₂ (M = Nb and Ta) vdW heterostructures exhibit flexible anode materials in rechargeable LIBs. The heterostructure with NbS₂ shows a higher specific capacity (528.25 mA h g⁻¹) than the TaS₂ heterostructure (392.15 mA h g⁻¹). Recently, metallic blue phosphorene/VS₂ hybrid structures have been explored as promising anode materials for high-performing LIBs with high theoretical specific capacities up to 1211.34 mA h g⁻¹ and low diffusion barrier of Li-ions in the range of 0.16-0.17 eV. Zhang et al. predicted the blue phosphorene/borophene heterostructure as a promising anode material for LIBs having a high specific capacity of 1019 mA h g⁻¹. Wang et al. observed C₃N/phosphorene heterostructure as an efficient anode material in LIBs (specific capacity ~ 468.34 mA h g⁻¹). Recently, Javadian et al. conducted a density functional investigation on defective phosphorene as an anode material for high-performance alkali-metal (Li, Na, and K) batteries. This modification of the single-layer phosphorene enhances the adsorption strength of the alkali metals. The diffusion barriers of the alkali metals get improved by point defects on the monolayer phosphorene (0.1 eV for Li, 0.03 eV for Na, and 0.02 eV for K). The theoretical storage capacity for the lithiated and sodiated composite systems increases from 865 mA h g⁻¹ (for pristine phosphorene) to 882.5 mA h g⁻¹ due to the point defect. Chen et al. studied transition metal (Cr, Mn, Fe, Co, and Ni) doped phosphorene as anode for the LIBs and observed Fe-doped phosphorene to have a theoretical capacity of 800 mA h g⁻¹. Hao et al. decorated an anode material by doping S-atom to the phosphorene monolayer having directional anisotropy to use it in Na- and K-ion batteries and found the
theoretical specific capacities of 431 and 215.5 mA h g$^{-1}$, respectively. Hence, these previous reports indicate that further modifications on pristine phosphorene can significantly improve its electrode characteristics in alkali metal-ion batteries. In this context, Yang et al. introduced two 2D monolayers in two different studies, namely, P$_3$S$_4$ and C$_3$S$_5$, which are structurally analogous to phosphorene. The electronic properties show that the P$_3$S monolayer is an indirect wide band gap (2.71 eV) semiconductor, whereas the C$_3$S is a quasi-direct band gap (1.98 eV) semiconductor. Both monolayers exhibit thermal and mechanical stability, anisotropy, and high carrier mobility. This research group has utilized the C$_3$S monolayer as a photocatalyst for water splitting. However, the unique structures and these calculated properties indicate the possible use of the monolayers in alkali metal-ion batteries which is yet to be explored. Being motivated by these studies, we first report computationally the P$_3$S and C$_3$S monolayers as efficient electrode materials in alkali metal (Li, Na, and K) -ion batteries with contemporary interest.

Herein, we have carried out a density functional theory (DFT) based study to find the possibility of utilization of two monolayers, namely, P$_3$S and C$_3$S, as efficient anode materials in alkali metal (Li, Na, and K)-ion batteries with improved electrochemical performances. Firstly, we have optimized both the pristine monolayers with P$_{54}$S$_{18}$ and C$_{54}$S$_{18}$ stoichiometries. Next, we have calculated the electronic structures of the monolayers, and our result matched the previous reports by Yang et al.$^{49-50}$ Furthermore, we have determined the charge accumulation and depletion zones from the charge-density difference (CDD) plots which locate the effective sites on the pristine sheets for the alkali metal-atom adsorption. To understand the adsorption of the alkali metal atoms on the pristine monolayer systems, we have calculated adsorption energies for the adsorption processes. Semiconductor-to-metal transitions are observed for both the P$_3$S and C$_3$S sheets from the electronic structure of the single alkali metal ion adsorbed system. This emergence of metallic nature, due to the adsorptions of alkali metal ions, promotes the composite systems to be used as electrodes in the MIBs. Both monolayer systems have significant diffusion energy barriers, such as the K-ion diffusion in the C$_3$S monolayer seem to be barrierless. We have determined that the maximum theoretical storage capacity (C) for the alkali metal ion adsorbed composite systems is highest for the K-adsorbed C$_3$S system of 1182.79 mA h g$^{-1}$. Furthermore, the calculated open-circuit voltage (OCV) values suggest that the alkali metal adsorbed composite systems can be used as suitable electrode materials in metal-ion batteries.

**DETAILS OF COMPUTATION**

All the calculations were carried out using density functional theory (DFT) as implemented in Viena Ab initio Simulation Package (VASP)$^{51-52}$. For the mutual interactions between ion cores and valence electrons, the projector-augmented wave (PAW) was applied as pseudopotential.$^{53}$ The plane-wave cut-off energy was set to 400 eV to calculate the wavefunctions. The exchange-correlation functional (E$_{xc}[\rho]$) was based on generalized gradient approximation (GGA) conjugated with Perdew-Burke-Ernzerhof (PBE)$^{54-55}$. To avoid any interaction between the unit cell and its periodic images, a vacuum of 20 Å was added along the z-direction. The Brillouin zone (BZ) was sampled for the geometrical relaxations with a Monkhorst-Pack (MP)$^{56}$ k-point grid of (3×3×1). As the PBE functional underestimates the band gap energy, a screen hybrid functional HSE06, by Heyd-Scuseria-Ernzerhof$^{57}$, with a denser k-point grid (15×15×1) was implemented to calculate the electronic structures. The vaspkit code$^{58-59}$ was used to generate the input k-path of the BZ for HSE06 calculation. The energy convergence
criterion for structural relaxations in the self-consistent field iteration step was set to $1 \times 10^{-6}$ eV. The geometries were relaxed until the force on all the atoms became less than 0.01 eV/Å. To consider the weak vdW interactions between the alkali metals and the P$_3$S and C$_3$S monolayers, Grimme's DFT-D3 dispersion correction$^{60}$ was implemented in all the calculations. The charge-density difference (CDD) plot and Bader charge analysis$^{61}$ were adopted to rationalize the charge transfer from the alkali metal ions to the 2D nanosheets. The nudged elastic band (CI-NEB) method$^{62}$ was performed with twelve intermediate images to find the energy barrier for the diffusion of the alkali metal ions. The post-processing calculations were carried out by using VTST tools$^{63}$.

RESULT AND DISCUSSION

The P$_3$S monolayer has a monoclinic symmetry with the P2/m space group, but the C$_3$S monolayer has a triclinic geometrical arrangement with the P1 space group. Yang et al. first theoretically predicted the P$_3$S and C$_3$S monolayer in 2021$^{49-50}$. The unit cell of the P$_3$S monolayer contains six P and two S atoms, whereas the C$_3$S monolayer contains six C and two S atoms. The optimized lattice constants are determined as, for the P$_3$S unit cell: $a = 6.04$ Å, $b = 6.41$ Å, $\alpha = 91.63^\circ$, $\beta = 90.04^\circ$, and $\gamma = 89.92^\circ$; and for the C$_3$S unit cell: $a = 4.44$ Å, $b = 5.63$ Å, $\alpha = 90.23^\circ$, $\beta = 90.92^\circ$, and $\gamma = 113.23^\circ$ (Table S1). There are 54 P and 18 S atoms required to model the $3\times3\times1$ supercell of the P$_3$S monolayer, whereas 54 C and 18 S atoms are required for the $3\times3\times1$ C$_3$S monolayer. The relaxed structures of the $3\times3\times1$ P$_3$S and C$_3$S monolayers

![Figure 1. Optimized structures of pristine $3\times3\times1$ (a) P$_3$S and (d) C$_3$S monolayers [top and side view] (The violet, yellow, and brown balls represent P, S, and C atoms, respectively), (b) and (e) are the electron localization function (ELF) plots of the P$_3$S and C$_3$S monolayers, respectively, (c) and (f) represent potential energy evolution during AIMD simulations of the pristine P$_3$S and C$_3$S monolayers, respectively, at 500K for 15 ps along with top and side view final geometries.](image)

monolayer contains six P and two S atoms, whereas the C$_3$S monolayer contains six C and two S atoms. The optimized lattice constants are determined as, for the P$_3$S unit cell: $a = 6.04$ Å, $b = 6.41$ Å, $\alpha = 91.63^\circ$, $\beta = 90.04^\circ$, and $\gamma = 89.92^\circ$; and for the C$_3$S unit cell: $a = 4.44$ Å, $b = 5.63$ Å, $\alpha = 90.23^\circ$, $\beta = 90.92^\circ$, and $\gamma = 113.23^\circ$ (Table S1). There are 54 P and 18 S atoms required to model the $3\times3\times1$ supercell of the P$_3$S monolayer, whereas 54 C and 18 S atoms are required for the $3\times3\times1$ C$_3$S monolayer. The relaxed structures of the $3\times3\times1$ P$_3$S and C$_3$S monolayers
are presented in Figure 1a and Figure 1d. In the P$_3$S monolayer, three types of P-P bond lengths are present- 2.26, 2.27, and 2.28 Å, almost identical to the 2.24 Å in phosphorene$^{64}$ and 2.27 Å in SiP$_2$$^{65}$. The P-S bond length is 2.16 Å, which can be compared to 2.33 and 2.15 Å in PS$_2$$^{66}$ and P$_2$S$_3$$^{67}$, respectively (Table S1). In the C$_3$S monolayer, the average C-C bond length is 1.44 Å, which is comparable to 1.42 Å in graphene$^{68}$; the C-S bond length is 1.78 Å, which is larger than the C-S bond in bulk CS$_2$ (1.54 Å)$^{69}$ and slightly smaller than that in CS monolayer (1.87 Å)$^{70}$, the distance between the nearest two S atoms (3.17 Å) is outside the S-S bond length range. The monolayer has a thickness of 2.28 Å (Table S1). The S atom in both the monolayers has six valence electrons (3s$^2$3p$^4$); two of them form chemical bonds with the neighboring two P atoms (in P$_3$S) and two C atoms (in C$_3$S), and the rest are the lone pair electrons. The nonplanarity inside the monolayers probably arises due to the repulsion of these lone pairs of S atoms. In multielectronic systems, the electron localization function (ELF) is used to map the amount of electron pair probability and spatial localization of electrons. We have calculated the ELF of pristine P$_3$S and C$_3$S sheets and presented them in Figure 1b and Figure 1e, respectively. ELF can also determine the charge transfer and the nature of chemical bonding inside any material. For the P$_3$S sheet (Figure 1b), the localized electron densities are at the center of each P-P bond, which evidences the strong covalent bonding. But, in the P-S bonds, the localized electrons are slightly separated from P to S atoms, which induces polar covalent bonds. For the C$_3$S sheet, the bond pairs of electrons are slightly shifted towards the S atoms due to the difference in electronegativity, which suggests the formation of polar covalent bonds, but the biphenyl C-C bonds are typical covalent in nature (Figure 1e). It is important to note that we have successfully reproduced the ELF plots of pristine P$_3$S and C$_3$S monolayers by Yang et al.$^{49-50}$

The synthesis viability and practical electrode application in metal-ion batteries are directly dependent upon the dynamical and thermal stability of a 2D structure. We have calculated the phonon frequencies of both pristine nanosheets to check the dynamical stability. The phonon band structures and projected density of states are presented in Figure S2(a-d). The absence of
any imaginary frequencies clearly evidences the dynamical stability of the pristine P$_3$S and C$_3$S monolayers. Furthermore, to check the high-temperature thermal stability, we have carried out ab-initio molecular dynamics (AIMD) simulation for both the supercell within the framework of the canonical ensemble (NVT) for the 15 ps with a molecular dynamic time step of 1 fs at 500 K. The energetical fluctuation with time (in fs) has been presented in Figure 1c and Figure 1f for P$_3$S and C$_3$S monolayers, respectively. The MD simulation results suggest that initially there is a slight fluctuation of potential energy with respect to the initial ground state energy of the relaxed structure of the pristine 2D structures, but both the systems equilibrated at around 3-5 ps. It is worth mentioning that there is hardly any structural distortion after both simulations, indicating sufficient thermal stability at elevated temperatures for both the pristine monolayers. Moreover, our predicted 2D sheets have sufficient dynamical and thermal stability for practical electrode utility in MIBs.

The rapid charging-discharging process and longer lifespan of any rechargeable cell are directly attributable to the high electronic conductivity of electrode material. The electronic band structure of the pristine P$_3$S and C$_3$S monolayers is calculated to understand the electronic conductivity of the materials. Firstly, using PBE functional, we obtain the monolayers to be wide-band semiconductors with an indirect band gap of 1.91 and 1.20 eV for the P$_3$S and C$_3$S monolayers, respectively. As the PBE functional underestimates the band gap value due to the self-iteration error, we have implemented the HSE06 level of calculation to get more accurate electronic structure. The HSE06 calculation changes the band gap of the P$_3$S and C$_3$S monolayers to 2.78 and 1.99 eV, respectively, and the results are in good agreement with the previous study (2.71 and 1.98 eV, respectively) by Yang et al.$^{49-50}$ In Figure 2(a-d) and Figure S1(a-d), we have shown the band structure, and total density of states (TDOS) calculated using HSE06 and PBE functional, respectively.

To investigate the adsorption capabilities of the P$_3$S and C$_3$S monolayers, firstly, we must identify the possible adsorption sites for the alkali metal atoms (Li, Na, and K) within the 2D sheets, and are shown in Figure 3(a) and 3(b), respectively. In the P$_3$S sheet, there are seven non-equivalent adsorption sites present as follows- i) T$_{P-S}$: top of the P-S bond, ii) T$_{P-P}$: top of the P-P bond, iii) T$_{P}$: top of the P atom, iv) T$_{S}$: top of the S atom, v) T$_{hP}$: top of the P-hexagon, vi) T$_{hPS}$: top of the PS-hexagon, and vii) T$_{BH}$: top of the buckled hollow site. But, in the C$_3$S sheet, there are six non-equivalent adsorption sites present as follows- i) T$_{C-S}$: top of the C-S bond, ii) T$_{C-C}$: top of the C-C bond, iii) T$_{C}$: top of the C atom, iv) T$_{S}$: top of the S atom, v) T$_{h}$: top of the hexagon, and vi) T$_{BH}$: top of the buckled hollow site. It is possible to locate electron-deficient regions inside both monolayers (likely preferred adsorption sites) by analyzing the plot of the electron
localization function (ELF plot; Figures 1b and 1e). For that, we have adsorbed single alkali metal atoms (Li, Na, and K) at the corresponding sites in both monolayers and studied the adsorption processes. While calculating the ground state energies of the monometalated systems, the DFT-D3 dispersion (Grimme's correction) is considered to implement the van-der Waals interaction between the alkali metals and the two-dimensional monolayers. To get the adsorption feasibility of the alkali metal atoms on the P$_3$S and C$_3$S monolayers, the adsorption energy per metal atom ($E_{ad}$) has been calculated by following the formula$^{15,71}$

$$E_{ad} = \frac{(E_{ML+M} - E_{ML} - nE_{M})}{n}$$  

where $E_{ML+M}$ be the calculated total energy of the metalated monolayers, $E_{ML}$ be the total energy of the pristine monolayers, $E_{M}$ is the energy of a single alkali metal atom, and $n$ represent the number of alkali metal adsorbed at the respective sites of the monolayer surfaces. The relaxed structures are shown in Figure S3(a-f). The $E_{ad}$ values are presented in Table S2,

![Figure 4](image)

Figure 4. Electronic properties (Band structure and total density of states) of the single alkali metal adsorbed P$_3$S and C$_3$S monolayers: (a-c) and (d-f) represent Li-, Na-, and K-adsorbed P$_3$S and C$_3$S systems, respectively. Fermi levels are set to zero.

and it is observed that the T$_{BH}$-site and the T$_S$-site in P$_3$S and C$_3$S, respectively, are energetically the most favored sites for alkali metal atom adsorption processes. In P$_3$S monolayer the $E_{ad}$ values for the Li-, Na-, and K-adsorption processes at the T$_{BH}$-site are found to be $-5.52$, $-5.62$, and $-6.18$ eV, respectively. However, in the C$_3$S monolayer, the $E_{ad}$ values for the Li-, Na-, and K-adsorption processes at the T$_S$-site are calculated to be $-5.02$, $-4.90$, and $-5.35$ eV, respectively. Hence, K atom adsorption is energetically the most favored process for both monolayer systems. The fundamental requirement of a material to be used as an electrode in a metal-ion battery is that the material must be metallic. The high electronic conductivity during
the charging-discharging cycle of a secondary storage system is directly associated with a material's metallicity. There have been reports earlier that the pristine material is either a small gap or a wide-gap semiconductor, but metallicity appears after the adsorption of metal ions\textsuperscript{12,72-73}. For that purpose, we have calculated the band structures and total density of states of the

![Diagrams](image)

Figure 5. CDD plots of the single alkali metal adsorbed P\textsubscript{3}S and C\textsubscript{3}S monolayers: (a-c) and (d-f) represent Li-, Na-, and K-adsorbed P\textsubscript{3}S and C\textsubscript{3}S systems, respectively [side and top view]. The isosurfaces value is set to 0.002e/Bohr\textsuperscript{3}.

single alkali metal adsorbed P\textsubscript{3}S and C\textsubscript{3}S composite systems. The band structures and TDOS in Figure 4(a-f) show that after single metalation, the wide-gap semiconductors (pristine P\textsubscript{3}S and C\textsubscript{3}S monolayer) transform into metallic systems with improved electrical conductivity. Moreover, the semiconductor-to-metal transition sounds promising for electrode application in metal-ion batteries.

After the metalation, the semiconductor-to-metal transition indicates charge transfer from the alkali metal atoms to the 2D monolayers at their corresponding adsorption sites. We have performed Bader charge analysis of the single metalated composite systems. The results are presented in Table S3. The Li, Na, and K atoms transfer 0.86, 0.84, and 0.87 e charge in the P3S monolayer and 0.86, 0.84, and 0.88 e charge in the C3S monolayer system, respectively. These values indicate the alkali metals' cationic state, which is crucial for effective intercalation. We have determined the charge-density difference (CDD) to provide a better understanding of the charge transfer processes using the following expression,\textsuperscript{74}

\[
\Delta \rho = \rho_{ML+M} - \rho_{ML} - \rho_{M}
\]

where \(\rho_{ML+M}, \rho_{ML}, \text{and } \rho_{M}\) are the charge densities of the alkali metal-adsorbed P\textsubscript{3}S and C\textsubscript{3}S monolayer, pristine P\textsubscript{3}S and C\textsubscript{3}S monolayer, and isolated alkali metal atom, respectively. The CDD plots are shown in Figure 5(a-f). The blue isosurfaces represent the charge depletion region, while the yellow isosurfaces indicate the charge accumulation. In Figure 5, the sharp
contrast between the two isosurfaces ((blue and yellow) strongly suggests the charge transfer from the alkali metals to the two-dimensional P$_3$S and C$_3$S sheets.

A metal-ion battery's performance largely depends on how easily a metal ion diffuses inside the 2D materials. The feasibility of diffusion is related to the diffusion energy barrier ($\Delta E_{\text{diff}}$), which means the energy required to migrate a metal ion between the favored adsorption sites. To exhibit as an efficient electrode in MIB, it must have a low $\Delta E_{\text{diff}}$ corresponding to high metal-ion mobility and excellent charging-discharging character. However, the $\Delta E_{\text{diff}}$ depends upon how the metal ions interact with the 2D monolayer. This energy barrier also determines the activation energy of the systems. We have used the climbing image-nudged elastic band (CI-NEB) method to determine the diffusion energy barrier and the minimum energy path (MEP) between the initial and final state of the system. This computational technique relaxes several intermediate images (geometries) along the MEP. After discovering phosphorene, researchers have been searching for 2D materials structurally analogous to phosphorene with considerably low diffusion barriers. Hao et al.$^{48}$ reported the S-doped phosphorene has Na and K diffusion barriers towards the armchair direction are 0.81 and 0.68 eV, whereas, towards the zigzag direction, are 0.14 and 0.08 eV, respectively. The pristine and B-doped black phosphorene exhibit Mg-diffusion barriers of 0.065 and 0.181 eV, respectively.$^{75}$ A low Li-diffusion barrier of 0.09 eV for the Fe-doped phosphorene as an anode material has been predicted from first-principle calculations.$^{47}$ These metal-ion diffusion barrier values indicate that doping on phosphorene can be a convenient way to achieve a low diffusion barrier. For that objective, firstly, we have calculated the diffusion energy barrier for the alkali metals (Li, Na, and K) in S-decorated phosphorene, i.e., P$_3$S monolayer. We have found the Li-, Na-, and K-migration barriers as 0.74, 0.26, and 0.57 eV, respectively. But, at the current time, these are not excellent results concerning the previously reported lower diffusion barriers. Thus, we have moved towards the C$_3$S monolayer, the structural analogue of the P$_3$S monolayer, to get better

Figure 6. Energy profile diagrams for the diffusion of single alkali metal atom inside P$_3$S and C$_3$S monolayers: (a-c) and (d-f) be the Li, Na, and K diffusion inside P$_3$S and C$_3$S sheets, respectively. There are twelve intermediate images have been considered.
results. By implementing the CI-NEB method, we have calculated the diffusion barriers for the alkali metals (Li, Na, and K)-adsorbed C$_3$S monolayers. Twelve intermediate image geometries have been considered between the initial and final structures during the calculations. The MEPs have been identified for the diffusion process inside the 2D monolayer. The computed diffusion barrier values are 0.68 eV for Li, 0.30 eV for Na, and almost barrierless (−0.06 eV) for the K-ion diffusion in the C$_3$S nanosheet. Our calculated K-ion diffusion barrier is comparable with the previously reported Li-migration barrier in holey carbon nitride (0.04 eV) as anode material\textsuperscript{71}. Hence, the P$_3$S and C$_3$S monolayers (analogous to phosphorene) can be used as electrode material in alkali metal-ion batteries.

The open-circuit voltage (OCV) of a MIB largely influences its practical utilization. The electrochemical behavior of a MIB does depend upon its electrode potential ($E_{cell}$) which is defined as, $E_{cell} = E_{catho} - E_{anode}$, where $E_{catho}$ and $E_{anode}$ are the electrode potential for the cathode and anode material, respectively. The higher the $E_{cell}$ value, the higher will be the spontaneous performance of the storage system. Thus, a high $E_{cathode}$ or low $E_{anode}$ value is desirable for the optimum functionality of the electrochemical cell. For the theoretical prediction of a system as an anode or cathode, OCV plays a pivotal role. Herein, the average OCV for the alkali metal adsorbed P$_3$S and C$_3$S composite systems have been determined by considering the following charging-discharging half-reaction,\textsuperscript{76}

$$P_{54}S_{18} + nM^{+1} + xe \leftrightarrow P_{54}S_{18}M_x \ (M = Li/Na/K) \quad (3)$$

$$C_{54}S_{18} + nM^{+1} + xe \leftrightarrow C_{54}S_{18}M_x \ (M = Li/Na/K) \quad (4)$$

The OCV of an electrode depends upon the change in Gibbs free energy ($\Delta G_f$) while adsorbing the metal ions; $OCV = -(\Delta G_f / xe)$, where $x$ is the number of alkali metals adsorbed on the P$_3$S and C$_3$S monolayers and $e$ is the charge of an electron. Further, $\Delta G_f$ can be represented as

![Figure 7. Voltage profile diagrams due to gradual increase of alkali metal atom in the P$_3$S and C$_3$S monolayers: (a-c) and (d-f) be the Li, Na, and K adsorbed P$_3$S and C$_3$S sheets, respectively.](image-url)
\[ \Delta G_f = \Delta E_f + PV - T\Delta S \] By ignoring the volume change (\(\Delta V\)) and the entropy effect (\(\Delta S\)), we get \(OCV = -\frac{\Delta E_f}{x_e}\) which can be calculated from the following equations,\(^{76}\)

\[
OCV\ (M@P_3S) = \frac{E_{P_{54}S_{18}} + xEM - E_{P_{54}S_{18}+xM}}{xe} \quad (M = Li/Na/K) \tag{5}
\]

\[
OCV\ (M@C_3S) = \frac{E_{C_{54}S_{18}} + xEM - E_{C_{54}S_{18}+xM}}{xe} \quad (M = Li/Na/K) \tag{6}
\]

where \(E_{P_{54}S_{18}}\) and \(E_{C_{54}S_{18}}\) are the ground state energies of pristine \(P_3S\) and \(C_3S\) monolayers \((3\times3\times1\) supercell\) respectively; \(E_{P_{54}S_{18}+xM}\) and \(E_{C_{54}S_{18}+x}\) are the ground state energies of alkali metal (M) adsorbed \(P_3S\) and \(C_3S\) monolayers, respectively; \(EM\) is the ground state energy of a single alkali metal atom (Li/Na/K) in crystalline bulk form; \(x\) and \(e\) are alkali metal concentrations in their adsorbed state and charge of an electron, respectively. For the Li-adsorbed \(P_3S\) systems, the OCV value decreases from 2.07 to 1.48 V (monolayer to tetralayer), which makes the average OCV of 1.75 V. For the Na-adsorbed \(P_3S\) systems, the OCV value decreases from 1.90 V to 1.80 V (monolayer to bilayer), that reports the average OCV of 1.85 V. The monolayer and bilayer K-adsorbed \(P_3S\) systems exhibit high OCV values of 2.28 and 2.27 V, respectively. The average OCV value increases from Li- to K-adsorbed \(P_3S\) composite systems, and the computed average OCV values are high. Materials having OCV values between 0.1 and 1.25 eV behave as an anode material, whereas materials with OCV values greater than 1.25 eV exhibit cathodic behaviour.\(^{13,15,71,77}\) However, presently, researchers are searching for efficient anode materials with OCV values less or equal to 1 V. Hence, these alkali metal adsorbed \(P_3S\) systems cannot be an excellent choice for anode materials; they can be used as cathode materials in an electrochemical device. Hence, in search of efficient anode materials, we have replaced the 2D sheet (\(P_3S\)) with a \(C_3S\) monolayer and calculated the OCV values. For the lithiated \(C_3S\) system, the OCV value decreases from 1.14 to 0.98 V in the monolayer to bilayer lithiated \(C_3S\). The OCV of the Na-adsorbed \(C_3S\) system decreases from 0.89 to 0.11 V in the monolayer to tetralayer. The K-atom forms a hexalayer with the \(C_3S\) nanosheet, accommodating 54 K-atom in its maximum adsorbed geometry. The OCV decreases from monolayer to hexalayer as 1.16 to 0.43 V. The increased metal-metal repulsion can explain the layer-by-layer voltage drop in multilayer-metallated systems over the 2D nanosheets (\(P_3S\) and \(C_3S\)). The plateaus in the voltage-profile diagrams (Figure 7) suggest stable and fruitful rechargeable batteries. Herein, we report the average OCV for the Li-, Na-, and K-adsorbed \(C_3S\) systems as 1.06, 0.43, and 0.81 V, respectively. The computed OCV values are comparable to the following reported systems: homogenous holey-\(C_3N_3\) monolayer for Li-ion battery (0.45 V),\(^{71}\) FeSe monolayer for Na-ion battery (0.49 V),\(^{78}\) 2D-bismuthine for K-ion battery (0.5 V),\(^{79}\) etc. Thus, we can expect the two-dimensional \(C_3S\) monolayer as a potential anode material for the alkali metal ion batteries with contemporary interests.

Besides OCV, theoretical storage capacity (C) is another crucial parameter contributing to a metal-ion battery's practicability. The throughput could be achieved if a practical facility continuously manufactured at its optimum efficiency. Theoretical storage capacity is the amount of current generated for the electrochemical reactions inside the cell, expressed in mA h g\(^{-1}\). To calculate the maximum theoretical storage capacity (C), first, we have determined the adsorption energies (\(E_{\text{ad}}\)) of the alkali metal atoms layer-by-layer on the surface of \((3\times3\times1)\) \(P_3S\) and \(C_3S\) systems by following the equations,
\[ E_{ad} (M@P_3S) = \frac{E_{P_{54}S_{18}+nM} - E_{P_{54}S_{18}} - \chi E_M}{n} \quad (M = Li/Na/K) \]  
(7)

\[ E_{ad} (M@C_{3S}) = \frac{E_{C_{54}S_{18}+n} - E_{C_{54}S_{18}} - \chi E_M}{n} \quad (M = Li/Na/K) \]  
(8)

where \( E_{P_{54}S_{18}+nM} \) and \( E_{C_{54}S_{18}+nM} \) are the ground state energies of alkali metal (M) adsorbed on the P\(_3\)S and C\(_3\)S monolayers, respectively; \( E_{P_{54}S_{18}} \) and \( E_{C_{54}S_{18}} \) are the ground state energies of pristine P\(_3\)S and C\(_3\)S monolayers, respectively; \( E_M \) is the ground state energy of a single alkali metal atom (Li/Na/K) in a bulk crystal; \( n \) represents the number of alkali metals adsorbed on the 2D monolayers. For the Li adsorption process, initially, we have adsorbed Li atoms on the most preferred sites on both the 2D systems. It is noticed that the lithiated monolayer of P\(_3\)S and C\(_3\)S can hold six and nine Li atoms, respectively. Both the lithiated monolayers are stable with adsorption energies of \(-2.07\) and \(-1.14\) eV, respectively. Further, we add six and nine more Li atoms at the bottom of the monolayer lithiated P\(_3\)S and C\(_3\)S systems to form a bilayer lithiated system. After geometrical optimization, the lithiated bilayer composite systems have \( E_{ad} \) values of \(-1.69\) and \(-0.98\) eV for P\(_3\)S and C\(_3\)S, respectively. Now, we design a tetralayer for the bilayer lithiated P\(_3\)S systems, and after relaxation, we obtain \(-1.48\) of adsorption energy. But, the lithiated tetralayer of C\(_3\)S is not energetically allowed. Thus, tetralayer and bilayer are the maximum adsorbed geometries for the Li-adsorbed P\(_3\)S and C\(_3\)S systems, respectively. The P\(_3\)S sheet adsorbs 24 Li atoms in its maximum adsorbed geometry, whereas the C\(_3\)S adsorbs 18 Li atoms. For the Na-adsorbed P\(_3\)S and C\(_3\)S composite systems, the Na atoms adsorb similarly to Li to form the monolayer. There are six Na atoms in the monolayer sodiated P\(_3\)S and nine Na atoms in C\(_3\)S, with the \( E_{ad} \) of \(-1.90\) and \(-0.89\) eV, respectively. The bilayer sodiated P\(_3\)S exhibits \( E_{ad} \) of \(-1.80\) eV, and this is the maximum adsorbed configuration with 12 Na-atoms. But, the C\(_3\)S is feasible to form a tetralayer sodiated state with the \( E_{ad} \) of \(-0.11\) eV.
eV, which is the maximum adsorbed geometry (36 Na-atoms). The K-atoms adsorb on the P$_3$S nanosheet like the Li- and Na-adsorption processes to form its maximum adsorbed geometry and bilayer k-adsorbed P$_3$S. But, the K-adsorption on the C$_3$S nanosheet is quite interesting. It forms a hexalayer of K-atoms as its maximum adsorption configuration with the $E_{ad}$ of $-0.43$

![Figure 9](image.png)

Figure 9. Potential energy evolution during AIMD simulations (500K-10ps) of the (a) tetralayer Li-adsorbed P$_3$S, (b) bilayer Na-adsorbed P$_3$S, (c) bilayer K-adsorbed P$_3$S, (d) bilayer Li-adsorbed C$_3$S, (e) tetralayer Na-adsorbed C$_3$S, and (f) hexalayer K-adsorbed C$_3$S along with the final geometries [top and side view] (The violet, brown, yellow, green, golden yellow, and purple balls represent P, C, S, Li, Na, and K atoms, respectively).

eV that accommodates 54 K-atoms. The monolayer, bilayer, and tetralayer K-adsorbed systems show $E_{ad}$ of $-1.16$, $-1.01$, and $-0.65$ eV, respectively. The layer-by-layer adsorption energies are systematically presented in Table S4. The optimized geometries of alkali metal adsorbed layered structures of P$_3$S and C$_3$S nanosheets are shown in Figures S4 and Figure S5, respectively. For the practical utility in MIB, the thermal stability of the layered metalated geometries is extremely important. For that, we have employed AIMD simulation of the alkali metal adsorbed layered structures of the C$_3$S systems at 500K for 10 ps with a 1 fs time step. The energy fluctuations with the time of the maximum adsorbed geometries have been shown in Figure 9(a-f). The final geometries and the energy fluctuations in potential energy-time plots suggest the thermal stability of the composites that may be used as anode materials in metal-ion batteries.

After studying the layer-by-layer adsorption processes, the maximum theoretical storage capacities have been calculated by using the following equation,

$$ C = \frac{z \times x_{max} \times F \times 10^3}{M} $$

where $M$ is the molar mass of the pristine 2D monolayer (P$_3$S / C$_3$S), $z$ is the valency of the adsorbed metal ion (1 for the alkali metal ions), $x_{max}$ is the number of alkali metals present in the highest populated geometries, and $F$ represents the Faraday constant (26.810 Ah/mol).
First, we have computed capacities for the P\textsubscript{3}S systems, and we obtain the following: $C_{\text{Li}\text{a}@P_3S} = 285.97$ mA h g$^{-1}$, $C_{\text{Na}@P_3S}$ and $C_{\text{K}@P_3S} = 142.98$ mA h g$^{-1}$. According to current needs in commercial markets, these theoretical capacities are very low in metal-ion batteries. Furthermore, we have calculated the maximum theoretical capacities for the alkali metal adsorbed C\textsubscript{3}S systems, and the results are fascinating. The Li and Na-based C\textsubscript{3}S systems exhibit moderate capacities as, $C_{\text{Li}@C_3S} = 394.26$ mA h g$^{-1}$ and $C_{\text{Na}@C_3S} = $ mA h g$^{-1}$. For the first time, the K-adsorbed C\textsubscript{3}S entity reports a high theoretical storage capacity of $1182.79$ mA h g$^{-1}$. Hence, it is expected that the C\textsubscript{3}S monolayer can discharge a greater amount of energy than the P\textsubscript{3}S monolayer in a single run. Our calculated capacities in C\textsubscript{3}S systems are more significant than some earlier reported anode materials such as $\text{Ti}_2\text{PX}_2$-Na (X = S, Se, and Te): 421 - 842 mA h g$^{-1}$; $\text{V}_3\text{C}_2$ MXene for Li, Na, K, and Ca metal ions: 269.86 - 606.42 mA h g$^{-1}$; $\text{Mo}_2\text{CrC}_2$ MXene for Li, Na, K, and Mg metal ions: 154.88 - 927.51 mA h g$^{-1}$.

The swelling and explosion of rechargeable batteries is a burning problem for practical users in their daily-life charging-discharging process. The volume expansion of the electrode material during electrochemical processes significantly impacts its commercialization on the consumer market. Hence, this issue must be addressed during the modeling of any electrode material for its practical use. To encounter the issue, we have determined the volume change of the pristine C\textsubscript{3}S monolayer and alkali metals (Li-, Na-, and K-) intercalated C\textsubscript{3}S sheet at their maximum adsorbed geometries and the results are presented in Table S4. The net volume increments for the Li-, Na-, and K-adsorbed P\textsubscript{3}S systems are 0.037%, 0.33%, and 0.41%, respectively, and for the C\textsubscript{3}S systems are 0.025%, 0.004%, and 0.006%, respectively. It is essential to mention that the calculated volume expansion values are significantly lower than the previously reported 2D Ti\textsubscript{3}C\textsubscript{2}O\textsubscript{2} anode (0.75%) for Na-ion batteries\textsuperscript{84} and 2D V\textsubscript{2}S\textsubscript{2}O (4.1%) for the K-ion batteries\textsuperscript{85}. However, the metalated C\textsubscript{3}S geometries expand comparatively lesser than the P\textsubscript{3}S systems. Thus, our predicted 2D anode materials are almost free of volume expansion issues and meet the safety requirement. In addition to the volume expansion factor, the alkali metals must not collate with each other to form a cluster at their most populated configurations. For that, we have determined the average Li-Li, Na-Na, and K-K distances after the AIMD simulation (500K-10ps) of those configurations and found them to be 3.12, 3.26, and 4.10 Å, and 3.17, 3.32, and 4.21 Å for the P\textsubscript{3}S and C\textsubscript{3}S systems, respectively. The average Li-Li, Na-Na, and K-K distances at their corresponding dimers are 2.72, 3.07, and 3.90 Å, respectively. Hence, the possibility of dimer formation at their maximum adsorption geometries is ruled out, and both 2D monolayers exhibit enhanced electrochemical behavior as potential anode materials in various alkali metal ion batteries.

**CONCLUSION**

In conclusion, we have assessed the viability of two-dimensional (2D) P\textsubscript{3}S and C\textsubscript{3}S monolayers as anode material for Li, Na, and K-ion batteries for the first time. We found the dynamical and thermal stability of the pristine 2D systems from the phonon calculation and AIMD simulation (500K-15 ps). By HSE06 level of electronic calculations, we have revealed that the pristine sheets are wide-band semiconductors with a band gap of 2.78 and 1.99 eV for P\textsubscript{3}S and C\textsubscript{3}S monolayers, respectively, which are in line with the earlier report quite well. Our findings indicate that the adatoms bind strongly to both the 2D monolayers at their favorable adsorption sites and undergo a substantial charge transfer, as evidenced by the Bader charge analysis and
charge-density difference (CDD) plots. With metalation, a semiconductor-to-metal transition is observed for all the composite systems, which sounds promising as an electrode application in metal-ion batteries. Also, we have explored that a single adatom diffuses readily inside the 2D structures. For instance, the diffusion of K on C₃S exhibits a low barrier value of 0.06 eV, which seems almost barrierless. After layer-by-layer alkali metal adsorption, the maximum adsorbed configurations are thermally stable, evidenced by the AIMD simulation at 500K for 10 ps. Our metalated hybrid systems show high theoretical capacities; for example, hexalayer K-adsorbed C₃S reports 1182.79 mA h g⁻¹. Furthermore, the calculated open-circuit voltage (OCV) values range from 1.75-2.27 and 0.43-1.06 eV for the P₃S and C₃S systems. The OCV values imply that P₃S composite systems should be used as cathode materials, and C₃S composite systems should be used as excellent anode materials. It is important to note that the maximum adsorbed geometries expand considerably low during the charging-discharging process. Hence, our predicted anode materials meet the safety issue in day-to-day applications. According to our investigation, the alkali metal adsorbed C₃S systems can be utilized as promising anode material for Li-, Na-, and K-ion batteries, and C₃S monolayer may be the best option for K-ion batteries among the other systems explored in this work.

**SUPPORTING INFORMATION**

Band structure and total density of states of pristine P₃S and C₃S monolayers (PBE calculation), phonon band structure and partial density of states for (3×3×1) pristine P₃S and C₃S monolayers, relaxed structures of the single alkali metal (Li, Na, and K) adsorbed P₃S and C₃S monolayers, optimized structures of the layered metallated P₃S and C₃S composite systems; structural information of pristine P₃S and C₃S monolayers in tabular form, adsorption energies \((\mathcal{E}_{\text{ad}})\) for the single alkali metal adsorbed P₃S and C₃S monolayers in tabular form, adsorption energies \((\mathcal{E}_{\text{ad}}\) for the single alkali metal adsorbed P₃S and C₃S monolayers, Bader charge analysis and diffusion barrier of the single alkali metal adsorbed P₃S and C₃S systems in tabular form, layer-by-layer \(E_{\text{ad}}\), average OCV, maximum theoretical capacities (C), and % volume expansion of the alkali metal adsorbed P₃S and C₃S systems in tabular form.
REFERENCES


