β-Arsenene Monolayer: A Promising Electrocatalyst for Anodic Chlorine Evolution Reaction

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Abstract: Materials innovation plays an essential role to address the increasing demands of gaseous chlorine from anodic chlorine evolution reaction (CER) in chlor-alkali electrolysis. In this study, two-dimensional (2D) semiconducting group-VA monolayers were theoretically screened for the electrochemical CER by means of the density functional theory (DFT) method. Our results reveal the monolayered β-arsenene has the ultralow thermodynamic overpotential of 0.068 V for CER, which is close to that of the commercial Ru/Ir-based dimensionally stable anode (DSA) of 0.08 V @ 10 mA cm⁻² and 0.13 V from experiments and theory, respectively. The change of CER pathways via Cl⁺ intermediate on 2D β-arsenene also efficiently suppresses the parasitical oxygen gas production because of a high theoretical oxygen evolution reaction (OER) overpotential of 1.95 V. Our findings may therefore expand the scope of the electrocatalysts design for CER by using emerging 2D materials.

Keywords: 2D group-VA monolayers; chlorine evolution reaction; electrocatalysis; selectivity

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To date, two-dimensional (2D) layered nanostructures have attracted increasing attention using as electrocatalysts, since they expose more active sites and achieve much higher catalytic efficiency [20–27]. Recently, the successful fabrication of few-layer black phosphorus brings group-VA elements (P, As, Sb, and Bi) into the family of 2D materials and inspires research interest on other layered allotropes [28]. For example, Bat-Erdene et al. reported that 2D antimonene nanosheets is an efficient electrocatalyst for the nitrogen reduction reaction (NRR) [29]. Additionally, Ren et al. adopt a favorable liquid exfoliation approach to produce few-layer antimonene and implement a metal-free electrocatalyst for water splitting [30]. Thus, the 2D semiconductor family, composed of group-VA elements, has a great potential for electrocatalysis. Yet, the investigations of this class of materials for the CER are still rare.

In this study, the density functional theory (DFT) was employed to comparatively investigate the CER electrocatalytic performance of 2D group-VA monolayers including phosphorene, arsenene, antimonene, and bismuthene. Here, considering the energetic stability and possible fabrication in experiments, we mainly focus on the α and β phases of group-VA monolayers [31–33]. Our DFT results predict that the 2D β-arsenene monolayer is a promising candidate for CER with the ultralow thermodynamic overpotential of 0.068 V and high selectivity in terms of OER.

2. Results and Discussion

2.1. Cl Adsorption on Group-VA Monolayers

The atomic structures of α and β phases of group-VA monolayers are shown in Figure 1. Their structural parameters are listed in Table 1. Group-VA monolayers with α and β allotropes possess honeycomb structures, where α and β phases are derived from orthorhombic and rhombohedral bulk structures, respectively. The lattice constants and layer thicknesses of all studied group-VA monolayers increase from P to Bi regardless of phase because of the increased atomic radius. For four monolayers with α phase, there are two types of bonds, namely in-plane bond (Bond 1) and out-plane bond (Bond 2), as shown in Figure 1a. It is found that bond lengths of both types gradually increase along the periodic table. For another allotrope β phases, only one type of bond, X–X, can be observed with bond lengths increasing from β-phosphorene (2.26 Å) to β-bismuthene (3.04 Å). All these structural parameters are consistent with reported data in previous studies [31,32].

![Figure 1](image_url)
Table 1. Structural parameters of all group-VA 2D monolayers. a and b are the lattice constants, d is the thickness of the monolayer, and L denotes the bond lengths.

| Phases | a (Å) | b (Å) | d (Å) | Bonds | L (Å) |
|--------|-------|-------|-------|-------|-------|
| P      | α     | 4.59  | 3.30  | 2.11  | in-plane 2.22, out-plane 2.26 |
|        | β     | 3.27  | 3.27  | 1.24  | P–P 2.26 |
| As     | α     | 4.70  | 3.69  | 2.41  | in-plane 2.51, out-plane 2.50 |
|        | β     | 3.60  | 3.60  | 1.40  | As–As 2.51 |
| Sb     | α     | 4.76  | 4.38  | 2.83  | in-plane 2.94, out-plane 2.86 |
|        | β     | 4.11  | 4.11  | 1.65  | Sb–Sb 2.89 |
| Bi     | α     | 4.90  | 4.58  | 2.99  | in-plane 3.09, out-plane 3.02 |
|        | β     | 4.33  | 4.33  | 1.73  | Bi–Bi 3.04 |

Previous theoretical and experimental studies of the electrocatalytic CER over low-dimensional anodes suggest that the formation of the Cl* intermediate instead of ClO* intermediate would significantly promote the chlorine generation with high selectivity [16–18,34]. Herein, to evaluate the CER performance of group-VA 2D monolayers, the adsorption properties of Cl atoms on both α and β phases were first investigated, and the results are listed in Table 2. As illustrated in Figure 1, one adsorption site (top) of α phase and three different adsorption sites including Site 1 (top), Site 2 (hollow), and Site 3 (hollow) of β phase were considered here to examine the regioselectivity of Cl atoms. It was found that the adsorption on the Site 2 of β-antimonene and Site 3 of β-phosphorene and β-arsenene is unpreferred because the adsorbed Cl atom would migrate to the Site 1 after structural optimization. Moreover, for 2D β-phosphorene and β-arsenene, the Cl adsorptions at Site 1 are much less positive than that of Site 2, indicating that Site 1 is thermodynamically preferred for chlorine adsorption. As a comparison, the Gibbs free energies of Cl* at the Site 3 on β-antimonene and β-bismuthene are much more negative than others, which implies that this hollow site is energetically favored for adsorbing Cl atoms.

Table 2. Calculated average distance between Cl and group-VA atoms (r_{Cl–X}), adsorption energy (ΔE_{Cl*}), and Gibbs free energy change (ΔG_{Cl*}) on different sites of group-VA 2D monolayers with α and β phases.

| α     | Structures | r_{Cl–X} (Å) | ΔE_{Cl*} (eV) | ΔG_{Cl*} (eV) |
|-------|------------|--------------|--------------|---------------|
| P     | Site 1     | 2.21         | −0.134       | 0.236         |
|       | Site 2     | 3.04         | 0.582        | 0.952         |
| As    | Site 1     | 2.37         | −0.302       | 0.068         |
|       | Site 2     | 3.07         | 0.271        | 0.641         |
| Sb    | Site 1     | 2.51         | −0.585       | −0.215        |
|       | Site 3     | 2.98         | −0.602       | −0.232        |
| Bi    | Site 1     | 2.59         | −0.797       | −0.427        |
|       | Site 2     | 3.20         | −0.799       | −0.429        |
|       | Site 3     | 3.08         | −1.091       | −0.721        |

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Table 2. Calculated average distance between Cl and group-VA atoms (r_{Cl–X}), adsorption energy (ΔE_{Cl*}), and Gibbs free energy change (ΔG_{Cl*}) on different sites of group-VA 2D monolayers with α and β phases.
2.2. CER Activity of Group-VA Monolayers

The electrocatalytic CER is a two-electron process through the Volmer-Heyrovsky mechanism [12,34]. By using the Cl* intermediate, this mechanism can be explained by that Cl* forms first via the adsorption and discharge of a chloride anion in the Volmer step (\( \text{Cl}^- + 2\text{e}^- \rightarrow \text{Cl}^* + \text{Cl}^- + \text{e}^- \)). Thereafter, the Cl* intermediate directly combines with another chloride anion from the electrolyte solution to release gaseous chlorine in the Heyrovsky step (\( \text{Cl}^* + \text{Cl}^- + \text{e}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \)). Figure 2 depicts the Gibbs free energy changes for CER with the most stable configurations of all monolayers with \( \alpha \) and \( \beta \) phases at the equilibrium potential of 1.36 V according to Volmer and Heyrovsky steps. The theoretical overpotential for CER (\( \eta_{\text{CER}} \)) can be defined by the \( \Delta G_{\text{Cl}^*} \), namely \( \eta_{\text{CER}} = \left| \Delta G_{\text{Cl}^*} \right| / e \). As shown in Figure 2, the interactions between Cl atoms and \( \alpha \)-monolayers are relatively stronger than that of \( \beta \)-monolayers due to the much more negative values of \( \Delta G_{\text{Cl}^*} \). In the case of \( \alpha \)-monolayers, the energy wells of \( \alpha \)-arsenene, \( \alpha \)-antimonene, and \( \alpha \)-bismuthene indicate that the Cl* can form spontaneously. However, the interactions between As, Sb, and Bi and Cl atoms are too strong for efficient Cl\(_2\) desorption. Consequently, the formation of Cl\(_2\) in the Heyrovsky step is energy-demanding for \( \alpha \)-arsenene, \( \alpha \)-antimonene, and \( \alpha \)-bismuthene with the thermodynamic overpotentials of \(-0.232\) V, \(-0.856\) V, and \(-0.966\) V, respectively. As a comparison, the small energy barrier for \( \alpha \)-phosphorene implies that the formation of Cl* in the Volmer step is more energy-demanding, leading to a theoretical overpotential of 0.055 V. It demonstrates that the CER mechanisms on \( \alpha \)-group VA monolayers can be adjusted by using different elements, and \( \alpha \)-phosphorene possesses the highest activity for Cl\(_2\) evolution among these materials.

![Figure 2](image_url)

Figure 2. Gibbs free energy diagrams for CER over (a) \( \alpha \) and (b) \( \beta \) phase of group-VA monolayers.

In addition, the CER performances of \( \beta \)-monolayers are quite distinct from \( \alpha \)-monolayers due to the totally different atomic structures. Specifically, \( \beta \)-phosphorene has relatively low activity ascribed to its weak binding ability with Cl, whereas \( \beta \)-antimonene and \( \beta \)-bismuthene are anticipated to possess low activity owing to the overly strong adsorption of Cl*. It is notable that \( \beta \)-arsenene has a moderate \( \Delta G_{\text{Cl}^*} \) of 0.068 eV to compromise the reaction barriers in the Cl adsorption and desorption steps, which is beneficial to generate Cl\(_2\) gas. As reported by Exner et al., the CER overpotential of the traditional single-crystalline RuO\(_2\) (110) electrocatalyst is 0.13 V vs. SHE via the ClO* precursor [12,14,35]. For better comparison, a summary table including the CER performance for reported electrocatalysts is listed in Table 3. Therefore, our DFT results suggest that the monolayered \( \alpha \)-phosphorene and \( \beta \)-arsenene exhibit comparable CER activity compared to that of benchmark RuO\(_2\) (110) electrocatalyst.
Table 3. Summary of the experimental ($\eta_{\text{exp}}$) and thermodynamic overpotentials($\eta_{\text{td}}$) of reported electrocatalysts for chlorine evolution $^a$.

| Electrocatalyst           | $\eta_{\text{exp}}$ (mV) @ 10 mA cm$^{-2}$ | $\eta_{\text{td}}$ (V) | Ref.     |
|--------------------------|---------------------------------------------|-------------------------|----------|
| commercial Ru/Ir-based   | 105 N/A                                     |                         | [34]     |
| RuO$_2$ (110)            | 82 N/A                                      | 0.13                    | [1,12,14,36] |
| Ru/Ir/TiO$_2$            | >240 N/A                                    |                         | [37]     |
| RuO$_2@$TiO$_2$          | ~80 N/A                                     |                         | [38]     |
| RuO$_2$TiO$_2$           | ~80 N/A                                     |                         | [39]     |
| Co$_3$O$_4$              | 200 N/A                                     |                         | [40]     |
| CoSb$_2$O$_x$            | ~300 N/A                                    |                         | [41]     |
| Pt/CNT                   | 50 N/A                                      | 0.09                    | [16,34]  |
| PtO$_2$ (110)            | N/A                                         | 0.20                    | [34]     |
| PtNT/CNT                 | 120 N/A                                     |                         | [34]     |
| β-arsenene               | N/A                                         | 0.068                   | This work |

$^a$ N/A—not available; CNT—carbon nanotube; NP—nanoparticle.

To deeply understand the CER performances of different group-VA monolayers with α and β phases, the bonding mechanism between the adsorbed Cl and P, As, Sb, or Bi atoms was investigated through the COHP and Mulliken charge analyses. The corresponding COHP images are shown in Figure 3, where covalent bonding and antibonding states are characterized by the positive and negative overlap population, respectively. For obtaining the quantitative description of covalent bonding strength between P, As, Sb, or Bi and Cl atoms, the integral of the $-$IpCOHP up to Fermi energy level was also calculated, shown in Figure 3. The more negative $-$IpCOHP value suggests that the corresponding active site is more reactive towards the adsorption of Cl via the covalent bonding. However, our results reveal that there is an inverse relationship between the $-$IpCOHP and $\Delta G_{\text{Cl*}}$, suggesting that the covalent bonding strength is not a reasonable descriptor for CER activity of α and β phases of group-VA monolayers. Therefore, we further investigate their ionic bonding strength, which can be described by the electrostatic attractions ($F_{es}$) between the P, As, Sb, or Bi and Cl atoms, as well as their bond length, as follows:

$$F_{es} = K \left| \frac{q_X \times q_{\text{Cl}}}{r_{\text{Cl-X}}^2} \right|$$  \hspace{1cm} (1)

where $K$ is Coulomb’s constant, and $q_X$ and $q_{\text{Cl}}$ are the Mulliken charges of group VA element $X$ ($X = P$, As, Sb, or Bi) and Cl, respectively, and the $r_{\text{Cl-X}}$ is the bond length between Cl and X atoms. As listed in Table 4, the trend of $-$IpCOHP values follows the rule of $P < As < Sb < Bi$ for all α- and β-monolayers, agreeing with the corresponding binding affinity of Cl atom. It demonstrates that the electrostatic attraction between group VA elements and Cl can be a reliable descriptor to predict the CER performance of all studied α- and β-monolayers, which is in agreement with our previous study [42].

To clearly visualize the X–Cl interaction, the electron localization function (ELF) of α- and β-monolayers with the Cl$^*$ was calculated, as displayed in Figure 4. The color denotes the renormalized ELF values, with the values 1.0 and 0.5 representing fully localized and fully delocalized electrons, respectively, while the value 0 means very low charge density. Since the electrons are gradually highly delocalized, it is found that the ionic bonding characters between X and Cl atoms increase with the increase of the atomic number. This can be ascribed to the gradually enhanced metallicity from P to Bi atoms, resulting from their decreased electronegativity. The atom with relatively strong metallicity would give rise to much stronger X–Cl interaction, such as Sb and Bi, which is detrimental to the desorption of Cl$_2$ gas. In contrast, the monolayers comprised of the non-metallic atom, such as α-phosphorene and β-arsenene, have the weaker X–Cl interaction to benefit the Cl desorption, resulting in the relatively high activity of Cl$_2$ generation.
where $K$ is Coulomb’s constant, and $q_X$ and $q_{Cl}$ are the Mulliken charges of group-VA element $X$ ($X = P, As, Sb, or Bi$) and Cl, respectively, and the $r_{Cl-X}$ is the bond length between Cl and $X$ atoms. As listed in Table 4, the trend of $−IpCOHP$ values follows the rule of $P < As < Sb < Bi$ for all $α$- and $β$-monolayers, agreeing with the corresponding binding affinity of Cl atom. It demonstrates that the electrostatic attraction between group-VA elements and Cl can be a reliable descriptor to predict the CER performance of all studied $α$- and $β$-monolayers, which is in agreement with our previous study [42].

Figure 3. COHP analyses of the chemical bonding between the adsorbed chlorine and group-VA element for (a) $α$-phosphorene; (b) $α$-arsenene; (c) $α$-antimonene; (d) $α$-bismuthene; (e) $β$-phosphorene; (f) $β$-arsenene; (g) $β$-antimonene; and (h) $β$-bismuthene monolayers, with the adsorbed Cl atom. The bonding and antibonding states are positive and negative of $−pCOHP$, respectively. The corresponding integral of $−pCOHP$ ($−IpCOHP$) values are also provided.

| Structures | $r_{Cl-X}$ (Å) | $q_{Cl}$ (e) | $q_X$ (e) | $F_{es}$ (eV/Å) |
|------------|----------------|--------------|-----------|----------------|
| A          |                |              |           |                |
| P          | 2.24           | −0.35        | 0.19      | 0.19           |
| As         | 2.39           | −0.43        | 0.20      | 0.22           |
| Sb         | 2.55           | −0.51        | 0.26      | 0.29           |
| Bi         | 2.70           | −0.56        | 0.29      | 0.32           |
| B          |                |              |           |                |
| P          | 2.21           | −0.29        | 0.25      | 0.21           |
| As         | 2.37           | −0.37        | 0.25      | 0.24           |
| Sb         | 2.51           | −0.44        | 0.35      | 0.35           |
| Bi         | 2.59           | −0.48        | 0.38      | 0.39           |
Figure 4. The electron localization functions for (a) α-phosphorene; (b) α-arsenene; (c) α-antimonene; (d) α-bismuthene; (e) β-phosphorene; (f) β-arsenene; (g) β-antimonene; and (h) β-bismuthene monolayers with the adsorbed Cl atom.

2.3. CER Selectivity

The evolution of gaseous oxygen at the anode is more thermodynamically preferred on account of the relatively lower potential $U_{\text{OER}}$ of 1.23 V vs. SHE, which regrettably causes the selectivity problem of Cl$_2$ gas production at the anode. Therefore, it should combine the high activity with selectivity in an acidic electrolyte for a desired CER electrocatalyst. Since the α-phosphorene and β-arsenene are predicted to have the best performance towards Cl$_2$ generation, the selectivity of these two monolayers for CER is further analyzed. According to the CHE method, the OER proceeds in the four-electron transfer steps, as follows:

$$\ast + H_2O \rightarrow HO^* + H^+ + e^-$$

$$HO^* \rightarrow O^* + H^+ + e^-$$

$$O^* + H_2O \rightarrow HOO^* + H^+ + e^-$$

$$HOO^* \rightarrow \ast + O_2 + H^+ + e^-$$

During the OER process, intermediates of HO*, O*, and HOO* are formed in turn following corresponding elementary steps. In this study, we used the adsorption free energy of HO* intermediate forming in the first elementary step of OER to evaluate the selectivity for α-phosphorene and β-arsenene monolayers. Figure 5a shows the Gibbs free energy changes of HO* and Cl* species of α-phosphorene and β-arsenene as a function of applied potential $U_{\text{SHE}}$ to determine the more energetically stable structures at pH = 0. It is observed that the value of $\Delta G_{\text{HO*}}$ of α-phosphorene monolayer is smaller than that of $\Delta G_{\text{Cl*}}$, implying that the formation of HO* intermediate on the α-phosphorene is more energetically favorable in acidic solution. This indicates that the OER process is preferred on the α-phosphorene monolayer at the potential region of $U_{\text{CER}}$, leading to a poor selectivity of Cl$_2$. As a comparison, the value of $\Delta G_{\text{Cl*}}$ of β-arsenene monolayer is much lower than that of $\Delta G_{\text{HO*}}$, suggesting that the CER process priors to the OER with the more thermodynamically favorable Cl* precursor.
The theoretical overpotential of OER is derived from the most energy-demanding step of four elementary reactions Equations (2)–(5). The reaction free energy of Equations (2)–(5) for OER can be defined as follows:

$$
\Delta G_1 = \Delta G_{HO^*} \\
\Delta G_2 = \Delta G_{O^*} - \Delta G_{HO^*} \\
\Delta G_3 = \Delta G_{HOO^*} - \Delta G_{O^*} \\
\Delta G_4 = 4.92 - \Delta G_{HOO^*}
$$

Therefore, the $\eta_{OER}$ can be calculated by

$$
\eta_{OER} = \frac{\max [\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]}{1.23}
$$

The formation of HOO* intermediate from O* is found to be the most endothermic step, resulting in the potential determining step (PDS) with an extremely large theoretical overpotential of 2.08 V at $U_{OER} = 1.23$ V. To be referenced to the same potential of CER ($U_{CER} = 1.36$ V), the corrected theoretical overpotential of OER for β-arsenene monolayer is 1.95 V, i.e., $\eta_{OER} = 2.08 - (1.36 - 1.23) = 1.95$ V. It reveals that the OER is efficiently suppressed on the 2D β-arsenene monolayer even in the absence of Cl-. In comparison, previous studies demonstrate that the widely used CER electrocatalyst RuO$_2$(110) is also highly active for oxygen evolution [43,44]. Our DFT results show that the thermodynamic OER overpotential of β-arsenene monolayer is five times larger than that of RuO$_2$(110) [12], indicating that the selectivity problem can be solved by using β-arsenene monolayer as the CER electrocatalysts. Such an improved selectivity of Cl$_2$ generation can be ascribed to the inherently different pathways for CER. Unlike RuO$_2$(110), by virtue of the ClO* intermediate, the CER on β-arsenene monolayer is via Cl species, which is beneficial to the selective chlorine evolution.

3. Computational Methods

All first principles DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) based on the projector-augmented wave (PAW) method [45,46]. The exchange-correlation energy was treated by the Perdew-Burke-Ernzerhof (PBE) functional at the generalized gradient approximation (GGA) level [47]. The electron-ion interaction was described using the PAW potentials [48], 3s$^2$3p$^3$ for P, 4s$^2$4p$^3$ for As, 5s$^2$5p$^3$ for Sb,
6s^25d^{10}6p^3 for Bi, 3s^23p^5 for Cl, 2s^22p^4 for O, and 1s^1 for H, respectively. In order to incorporate the effects of nonlocal van der Waals interactions that are not included correctly in conventional DFT calculations, the DFT-D3 method was adopted for dispersion corrections here [49–53]. A plane-wave basis set with the cut-off kinetic energy of 520 eV is employed to expand the smooth part of wave functions. The gamma-centered k-point meshes with a reciprocal space resolution of $2\pi \times 0.03$ Å$^{-1}$ and $2\pi \times 0.02$ Å$^{-1}$ were utilized for structural optimization and static self-consistent calculations, respectively. To model the $\alpha$ and $\beta$ phases of group-VA monolayers in this study, a $(3 \times 3)$ supercell was adopted, including 36 and 18 group-VA element atoms for $\alpha$ and $\beta$ phases monolayers, respectively. A 20 Å vacuum along z-direction was applied to prevent spurious interaction between the periodically repeated images. All atoms were allowed to relax until the Hellmann–Feynman forces were smaller than 0.01 eV/Å, and the convergence criterion for the electronic self-consistent loop was set to $10^{-5}$ eV. The projected crystal orbital Hamilton population (pCOHP) method was used via the LOBSTER program to understand the chemical bonding between group-VA elements (P, As, Sb or Bi) and adsorbed Cl atoms [54–58].

The adsorption energy ($\Delta E$) of all considered adsorbates (i.e., Cl*, HO*, O*, and HOO*, * refers to the corresponding catalytic site) can be calculated by following equations:

$$\begin{align*}
* + H_2O &\rightarrow O* + 2(H^* + e^-) \\
* + H_2O &\rightarrow HO* + H^* + e^- \\
* + 2H_2O &\rightarrow HOO* + 3(H^* + e^-) \\
* + Cl^- &\rightarrow Cl* + e^-
\end{align*}$$

Hence, $\Delta E$ for each species was calculated as follows:

$$\begin{align*}
\Delta E_{O*} &= E_{O*} + E_{H_2} - E* - E_{H_2O} \\
\Delta E_{HO*} &= E_{HO*} + 0.5E_{H_2} - E* - E_{H_2O} \\
\Delta E_{HOO*} &= E_{HOO*} + 1.5E_{H_2} - E* - 2E_{H_2O} \\
\Delta E_{Cl*} &= E_{Cl*} - E* - 0.5E_{Cl_2}
\end{align*}$$

The free energy change ($\Delta G$) of the considered adsorbates (i.e., Cl*, HO*, O*, and HOO*) was obtained by using the computational hydrogen electrode (CHE) method [59], which can be explained as follows:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

where $\Delta ZPE$ is the change in zero-pint vibrational energy and $-T\Delta S$ is the entropy contribution at room temperature. In this study, we considered the standard conditions of $a_{Cl^-} = 1$ and pH = 0. Therefore, the $\Delta G$ for each species as a function of applied potential $U_{SHE}$ can be defined as follows at 298 K:

$$\Delta G (U) = \Delta E + \Delta ZPE - T\Delta S - \nu(e^-) \cdot e \cdot U_{SHE} - \nu(Cl^-) \cdot e \cdot U_{Cl}$$

where $\nu(e^-)$, and $\nu(Cl^-)$ are the values for stoichiometric coefficient of transferred electrons and chloride of corresponding adsorption intermediates, respectively; $U_{Cl}$ is the standard potential of the reversible chlorine electrode (1.36 V at 298 K); and $U_{SHE}$ denotes the applied electrode potential referenced to standard hydrogen electrode (SHE).

4. Conclusions

In summary, the first-principle DFT calculations were performed to investigate the CER performance of 2D $\alpha$ and $\beta$ phases of group-VA monolayers. Our calculated results reveal that $\beta$-arsenene monolayer exhibits high activity and selectivity of gaseous Cl$_2$ generation by virtue of the expected Cl* precursor, with the thermodynamic overpotential.
of 0.068 V and 1.95 V for the CER and OER, respectively. This 2D β-arsenene monolayered catalyst may therefore be a promising candidate for CER in the acidic medium. Moreover, our results found that the COHP analyses fail to predict the CER performance of these α and β phases of group-VA monolayers, since the covalent bonding state between adsorbent and Cl atoms becomes weaker from P to Bi. The electrostatic attraction between adsorbent and Cl atoms is a better descriptor for these systems. The theoretical prediction of this study may broaden the scope of CER electrocatalysts design using 2D materials.

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