M$_2$X Monolayers as Anode Materials for Li Ion Batteries

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Electrochemically efficient electrode materials are required for clean energy storage in Li ion batteries. We predict two-dimensional hexagonal metal nitrides, borides, and phosphides (Sc$_2$B, Sc$_2$N, Y$_2$B, Y$_2$N, and Y$_2$P) and evaluate the feasibility of experimental realization. The materials combine excellent metallicity, as required for electrodes, with Li binding energies providing high storage capacity and a low average open-circuit voltage. In contrast to two-dimensional silicene, borophene, and SnS$_2$, we observe negligible structural distortions during Li adsorption and extraction, which results in high reversibility and a long cycle life. Superionic Li diffusion enables fast charge or discharge of next-generation Li ion batteries.

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I. INTRODUCTION

Rechargeable Li ion batteries (LIBs) play a crucial role as the power supply of electric vehicles and portable electronics, providing high energy density, high power rate, long cycle life, and low self-discharge [1,2]. The electrochemical performance depends on the anode, cathode, and electrolyte, which can be optimized individually to a large extent [3]. Concerning anodes, the storage capacity of conversion and alloying anodes is usually higher than that of intercalation anodes but a limited cyclability precludes commercial use [4–7]. Graphite, the conventional anode material of commercial LIBs, provides a storage capacity of 372 mAh/g due to reversible intercalation of Li ions in the layered structure [4]. Two-dimensional graphene, on the other hand, suffers from weak Li binding (low storage capacity), which can be enhanced through defects only by sacrificing the Li diffusion [8–11]. Graphene composite materials [12–14] presumably will be too expensive for usage in commercial LIBs. Other two-dimensional materials face issues of structural distortions during Li loading, weak Li binding, low metallicity, and/or slow Li diffusion [15–17]. Black arsenic [18] and MoO$_2$, MoS$_2$, MoSe$_2$,WO$_2$, WS$_2$, and WSe$_2$ [19,20] monolayers lack electronic conductivity and/or suffer from poor cyclability [21,22].

Two-dimensional metal carbidel and metal nitrides (Mo$_2$C, W$_2$C, Mo$_2$N, etc.) provide high stiffness, high electronic and ionic mobilities, high Li storage capacity, and superionic conductivity (which enables low charge or discharge times and high power rates) [23–29]. In the present study, we predict the related Sc$_2$B, Sc$_2$N, Y$_2$B, Y$_2$N, and Y$_2$P monolayers and evaluate their application potential in LIBs. Experimental feasibility of synthesis is demonstrated in terms of cohesive energies, phonon spectra, and mechanical and thermal stabilities. The Sc$_2$N and Y$_2$N monolayers exhibit suitable Li binding energies for high Li storage capacity. Negligible structural changes during Li loading, low average open-circuit voltage, excellent metallicity, and superionic Li diffusion make them highly promising anode materials for LIBs.

II. METHODS

First-principles calculations within the framework of density-functional theory are used to predict the structural, electronic, and Li adsorption and diffusion properties [30–32], employing the projector-augmented-wave method of the Vienna ab initio simulation package [33]. The electron exchange-correlation interaction is modeled in the generalized gradient approximation (Perdew-Burke-Ernzerhof functional) and the van der Waals interaction is taken into account by the method of Ref. [34]. The energy cutoff of the plane-wave expansion is set to 520 eV and for structure optimization a force criterion of 0.001 eV/Å is used. Each slab model contains a vacuum layer of 15 Å thickness in the out-of-plane direction and Γ-centered 25 × 25 × 1 k meshes [35] are used for Brillouin-zone integration. The PHONOPY code is used to calculate phonon spectra [36]. The elastic constants are obtained by the stress-strain approach [37]. Ab initio molecular dynamics simulations are conducted for 6 × 6 × 1 supercells of the M$_2$X monolayers using a canonical ensemble and the Nosé-Hoover thermostat. Also, 3 × 3 × 1 supercells to achieve low Li coverage are used for studying the Li
adsorption and determining the saddle points and minimum energy Li diffusion pathways by the climbing-image nudged-elastic-band method [38].

III. RESULTS AND DISCUSSION

As two-dimensional metal carbides and metal nitrides realize either 1T or 2H hexagonal structures [24–27,39], we consider both of these possibilities for the Sc2B, Sc2N, Y2B, Y2N, and Y2P monolayers. We find in each case that the 1T structure is energetically favorable and therefore we study it in the following. The obtained lattice parameters are given in Table I together with the energy differences compared with the corresponding 2H structures. We find in quasiharmonic approximation that a temperature of 300 K alters the lattice parameters by less than 0.03 Å.

We determine the cohesive energy as $E_{\text{coh}} = \frac{2EM + EX - EM_2X}{3}$, where $EM$ and $EX$ are the spin-polarized total energies of isolated $M$ and $X$ atoms, respectively, and $EM_2X$ is the total energy of the $M_2X$ monolayer. The results are given in Table I. They are compared to results for the MoS2 and SnS2 monolayers obtained by the same methodology.

The phonon spectra in Figs. 1(b)–1(f) show three acoustic and six optical modes, demonstrating dynamical stability of the $M_2X$ monolayers due to the absence of negative frequencies. For the Y2P monolayer, we also find dynamical stability for the 2H structure. The obtained elastic constants ($C_{11}$, $C_{12}$), the Young’s moduli ($Y$), and the Poisson ratios ($\nu$) are given in Table I. The Young moduli show that the stiffness of the Sc2N monolayer exceeds that of the MoS2 monolayer, while the results for the other $M_2X$ monolayers fall between those of the SnS2 and MoS2 monolayers. All monolayers satisfy the Born criteria of mechanical stability ($C_{11} > 0$, $C_{11} > |C_{12}|$) [40]. Ab initio molecular-dynamics simulations conducted for the Sc2N and Y2N monolayers (which provide suitable Li binding energies, see below) prove thermal stability at 300 K [see Figs. 2(a) and 2(b)], as the structures are conserved even after 6 ps of simulation time. For the layered bulk phases of Sc2N and Y2N (Fig. S1 [41]) with P3m1 symmetry, we obtain cleavage energies (energy difference between the bulk phase per layer and the isolated layer) of 0.32 and 0.24 Jm$^{-2}$, respectively, after optimization of the lattice parameters ($a = 3.20$ Å and $c = 5.35$ Å for Sc2N with an interlayer distance of 2.90 Å; $a = 3.47$ Å and $c = 5.91$ Å for Y2N with an interlayer distance of 3.25 Å). These values are significantly smaller than the cleavage energy of 2.15 Jm$^{-2}$ of the experimentally exfoliated

<table>
<thead>
<tr>
<th>$a$</th>
<th>$E_{\text{coh}}$</th>
<th>$\Delta E$</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$Y$</th>
<th>$\nu$</th>
<th>$E_{\text{H}}^T$</th>
<th>$E_{\text{T}}^T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS2</td>
<td>3.18</td>
<td>5.28</td>
<td>0.85</td>
<td>132.5</td>
<td>32.8</td>
<td>124.4</td>
<td>0.24</td>
<td>...</td>
</tr>
<tr>
<td>SnS2</td>
<td>3.69</td>
<td>3.67</td>
<td>-0.86</td>
<td>82.5</td>
<td>29.1</td>
<td>72.2</td>
<td>0.35</td>
<td>...</td>
</tr>
<tr>
<td>Sc2B</td>
<td>3.61</td>
<td>3.82</td>
<td>-0.87</td>
<td>83.6</td>
<td>26.5</td>
<td>75.2</td>
<td>0.32</td>
<td>-111</td>
</tr>
<tr>
<td>Sc2N</td>
<td>3.18</td>
<td>5.43</td>
<td>-0.57</td>
<td>135.7</td>
<td>36.6</td>
<td>125.8</td>
<td>0.27</td>
<td>-524</td>
</tr>
<tr>
<td>Y2B</td>
<td>3.84</td>
<td>3.79</td>
<td>-0.72</td>
<td>67.7</td>
<td>24.0</td>
<td>59.2</td>
<td>0.36</td>
<td>-30</td>
</tr>
<tr>
<td>Y2N</td>
<td>3.41</td>
<td>5.36</td>
<td>-1.23</td>
<td>117.0</td>
<td>34.6</td>
<td>106.8</td>
<td>0.29</td>
<td>-276</td>
</tr>
<tr>
<td>Y2P</td>
<td>3.78</td>
<td>4.75</td>
<td>-0.66</td>
<td>85.3</td>
<td>23.8</td>
<td>78.7</td>
<td>0.28</td>
<td>-109</td>
</tr>
</tbody>
</table>

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ReS\textsubscript{2} monolayer [42]. In contrast to many two-dimensional materials, the electronic band structures of the $M_2X$ monolayers in Fig. 3 demonstrate excellent metallicity, which is one of the most important requirements of an anode material.

We now study the Li storage capacity, the structural distortions during Li adsorption, the average open-circuit voltage, and the Li diffusion barrier. The Li binding energy is defined as $E_b = E_{M_2X+Li} - E_{M_2X} - E_{Li}$, where $E_{M_2X+Li}$ and $E_{M_2X}$ are the total energies of the $M_2X$ monolayer with and without the Li atom adsorbed, respectively, and $E_{Li}$ is the total energy of an isolated Li atom. Figures 4(c) and 4(d) show, for the Sc\textsubscript{2}N and Y\textsubscript{2}N monolayers, top and side views of $\Delta\rho$ for Li adsorption at the T site, demonstrating a large charge transfer (0.87 and 0.82 electrons, respectively, according to Bader analysis).

We calculate the average Li adsorption energy (total energy difference per atom before and after loading) to estimate the Li storage capacity, considering simultaneous adsorption on both sides of the monolayer as well as the possibility of multilayer adsorption. For this purpose, we employ a $2 \times 2 \times 1$ supercell and assume that volume and entropy effects are negligible during the adsorption. The Li atoms occupy H sites in the first layer and T sites in the second layer. As eight atoms can be accommodated in each Li layer, we define the average Li adsorption energy of the $n$th layer as $E_{av}(n) = \frac{(E_{M_2X+8nLi} - E_{M_2X+(n-1)8Li} - 8E_{Li})/8}{n}$, where $E_{M_2X+8nLi}$ and $E_{M_2X+(n-1)Li}$ are the total energies of the $M_2X$ monolayer loaded with $n$ and $n - 1$ Li layers, respectively, and $E_{Li}$ is the total energy of an atom in the body-centered-cubic structure of bulk Li. For the Sc\textsubscript{2}N monolayer, we obtain for the first, second, and third Li layers (Fig. S2 [41]) values of $-458$, $-22$, and $-8$ meV, respectively. The fact that $E_{av}$ becomes positive

FIG. 2. The temperature (black) and total energy (blue) during the \textit{ab initio} molecular-dynamics simulations of the (a) Sc\textsubscript{2}N and (b) Y\textsubscript{2}N monolayers at 300 K. The insets show the atomic structures after 6 ps of simulation time.

FIG. 3. The electronic band structures (spin-orbit coupling included) of the $M_2X$ monolayers: (a) Sc\textsubscript{2}B; (b) Sc\textsubscript{2}N; (c) Y\textsubscript{2}B; (d) Y\textsubscript{2}N; (e) Y\textsubscript{2}P.
(a) (b)

FIG. 4. Top and side views of the (a) H and (b) T adsorption sites and the valence-charge-density difference induced by Li adsorption on the (c) Sc2N and (d) Y2N monolayers (yellow, charge accumulation; blue, charge depletion; isovalue = 10⁻³ electrons/Å³).

for the fourth Li layer shows that a maximum of three Li layers can be stored (Li₆Sc₂N). For the Y₂N monolayer, we obtain only for the first Li layer a negative value of -255 meV, implying that only one Li layer can be stored (Li₂Y₂N).

The Li storage capacity is defined as \( C = xzF/M \), where \( x \) is the number of Li ions stored per formula unit, \( z = 1 \) is the ionic charge, \( F = 26801 \text{ mAh/mol} \) is the Faraday constant, and \( M \) is the molar mass of the \( M₂X \) monolayer. We obtain 1547 mAh/g for the Sc₂N monolayer and 279 mAh/g for the Y₂N monolayer. The Li storage capacity of the Sc₂N monolayer thus clearly exceeds literature reports for the MXenes Mo₂C (526 mAh/g) [25] and Ti₃C₂ (320 mAh/g) [43], the transition-metal dichalcogenide TiS₂ (479 mAh/g) [44], and the heterostructures MoS₂/VS₂ (584 mAh/g) [15] and MoS₂ per graphene (338 mAh/g) [45]. Moreover, the average open-circuit voltage \( V_{av}(n) = E_{av}(n)/e \) ranges between 0.46 and 0.02 V for the Sc₂N monolayer and amounts to 0.22 V for the Y₂N monolayer. These low values are favorable for high-voltage LIBs.

While the alloying mechanism gives rise to the highest Li storage capacities, graphite (insertion mechanism [4,5,7]) is still the first choice for commercial LIBs because of its high reversibility and long cycle life. Generally, structural changes in the anode material during lithiation and delithiation reduce the reversibility and the cycle life. In the cases of the SnS₂ and TiS₂ monolayers, the presence of Li affects the Sn—S and Ti—S bonds, respectively, and leads to decomposition [44–46]. Silicene behaves similarly [47]. On the contrary, we find even for fully lithiated Li₆Sc₂N that the Sc—N bond length remains unaltered, which guarantees high reversibility and a long cycle life. Electron localization functions calculated for the Sc₂N and Y₂N monolayers with one adsorbed Li layer are shown in Fig. 5. We observe metallic bonding between the Li atoms, which boosts the Li diffusion at high coverage.

The charge or discharge time and power rate of a LIB depend on the electron transport and Li diffusion properties of the anode material. The reversible electrochemical reaction taking place during charge or discharge can be written as \( M₂X + xLi^+ + e^- \rightleftharpoons Li_xM₂X \), with the Li⁺ ions moving through the high-band-gap liquid electrolyte between the electrodes and the electrons moving through the outer

(a) (b)

FIG. 5. The electron localization functions of the (a) Sc₂N and (b) Y₂N monolayers with one adsorbed Li layer.

(a) (b)

FIG. 6. The total densities of states (3 × 3 × 1 supercell, spin-orbit coupling included) of the (a) Sc₂N and Li₁Sc₂N and (b) Y₂N and Li₁Y₂N monolayers. The Fermi energy is set to 0 eV.
circuit of the battery. Thus, excellent metallicity and fast Li diffusion are key features of an efficient electrode material. Figure 6 shows the total densities of states obtained for the Sc$_2$N, Li$_2$Sc$_2$N, Y$_2$N, and Li$_2$Y$_2$N monolayers, demonstrating metallicity with and without adsorbed Li atoms. Therefore, no metallic additives are required, which is an important advantage, as such additives lower the Li diffusion and result in experimental complications that increase the price of the LIB [13,15,46,48–50].

Figures 7(a) and 7(b) show the relative energy along two Li diffusion pathways between T sites. The trajectories of the pathways are depicted as insets. While the direct pathway (T-T) results in Li diffusion barriers of 76 and 103 meV for the Sc$_2$N and Y$_2$N monolayers, respectively, we obtain values of only 19 and 27 meV for the minimum energy pathway (T-H-T). These values are one order of magnitude lower than reported for graphene and its derivatives [9–11], silicene [14], transition-metal monochalcogenides [51], and transition-metal dichalcogenides [15,52]. They are even lower than reported for most MXenes [25,27,53]. We observe no significant variation in the monolayer thicknesses and $M$—$X$ bond lengths during Li diffusion, which contributes to the low Li diffusion barriers. The smooth potential surface due to avoided formation of ionic $M$—Li bonds (Fig. 5) promotes the Li diffusion and gives rise to superior anode materials for LIBs.

IV. CONCLUSIONS

Sc$_2$B, Sc$_2$N, Y$_2$B, Y$_2$N, and Y$_2$P monolayers are predicted to be stable two-dimensional materials with hexagonal symmetry. All turn out to combine high stiffness with excellent metallicity. The Sc$_2$N and Y$_2$N monolayers provide Li binding energies suitable for application in LIBs. In particular, the high Li storage capacity (1547 mAh/g) and low Li diffusion barrier (19 meV) of the Sc$_2$N monolayer outperform competing anode materials including graphite (372 mAh/g [54], 0.48 eV [55]). Low Li diffusion barriers enable fast charge or discharge and high power rate, while negligible structural changes during lithiation and delithiation enable high reversibility and a long cycle life. In addition, low average open-circuit voltages pave the way for high-voltage LIBs. Overall, the remarkable electrochemical properties of the Sc$_2$N and Y$_2$N monolayers point to outstanding potential as anode materials in future LIB technology.

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