Theoretical Understanding of Mechanisms of Proton Exchange Membranes Made of 2D Crystals with Ultrahigh Selectivity

Le Shi,*† Ao Xu,‡ Guanhua Chen,§ and Tianshou Zhao*,†

†Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China
‡Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China
§School of Engineering, The Chinese University of Hong Kong, Shatin, Hong Kong, China

Supporting Information

Abstract: Recent reports on proton conduction across pristine graphene and hexagonal boron nitride (h-BN) provide a new avenue for the design of proton exchange membranes. The uniform pores formed by the electron clouds of two-dimensional (2D) crystals can effectively block the undesired transportation of other species thus ultrahigh selectivity can be achieved. With the aid of first-principles calculations, we investigate the proton conduction process across six kinds of intact 2D crystals, namely graphene, h-BN, β12 boron sheet, X3 boron sheet, phosphorene, and silicene. To clarify the proton conduction mechanism, three proton penetration modes are proposed: dissociation-penetration, adsorption-penetration, and direct penetration. Based on our calculation results, for graphene and h-BN without atomic defects, they are unlikely to provide sufficient proton conductivity at room temperature when no bias potential is applied. By contrast, the β12 boron sheet, X3 boron sheets, and silicene exhibit relatively lower proton penetration energy barriers, making them prospective candidates for future proton exchange membrane applications.

Due to their atomically thin structure, two-dimensional (2D) materials have emerged as a new family of building blocks for membranes which are expected to achieve low transport resistance as well as high selectivity.1–5 Most of previous works concentrated on creating pores on 2D materials to achieve desired selectivity for gas6–9 or ion separation.10–14 Significant progress have also been achieved on employing the graphene oxide nanosheets to serve as the selective proton exchange membranes.15–17 Recently, Geim’s group reported that the pristine 2D crystals, graphene, and hexagonal boron nitride (h-BN), can conduct protons via the uniform pores formed by the in-plane electron clouds with low energy barriers (0.78 eV for graphene and 0.30 eV for h-BN), thus can be used as proton exchange membrane in fuel cells18 and isotope separation devices.19 Follow-up experiments by our group20 and Holmes et al.21 also demonstrated that when sandwiching a chemical vapor deposition (CVD) grown graphene or h-BN layer in Nafion membrane, the methanol crossover issue in direct methanol fuel cells (DMFCs) can be significantly suppressed.

However, how protons conduct across 2D crystals in aqueous environment is still unclear, and whether intact graphene or h-BN can provide sufficient proton conductivity is under debate. Some researchers argue that the observed proton conductivity mainly come from the rare atomic defects.22,23 First-principles calculations have shown that, in a vacuum environment, if the protons penetrate graphene or h-BN via a metastable physiosorption state, the energy barriers are about 1.25–1.56 eV for graphene and 0.70–0.91 eV for h-BN, a bit higher than those deduced from experiments. Considering other factors such as the quantum nuclear effects (QNEs), bias potential and hydrogen adsorption, the proton penetration energy barriers can be further lowered, which may explain the experimental observations. However, if considering the much more stable chemisorption state of proton, the calculated energy barriers would be much higher (>3.0 eV).26 Moreover, the experiments were conducted in aqueous environment where the protons mainly exist in the form of hydronium ions (H3O+) instead of bare protons (H+), thus the vacuum environment assumption in previous calculations is oversimplified. Calculations incorporating explicit water molecules shown that the proton penetration in aqueous environment across intact graphene or h-BN is nearly impossible at room temperature with energy barriers higher than 3.0 eV, where a proton is assumed to first dissociate from a hydronium ion and then penetrate the 2D crystals and combine with another water molecule to form a new hydronium ion.27 Other possible proton penetration modes or other 2D crystals that exhibit lower proton penetration energy barriers are still yet to be explored.

In this Letter, we investigate the proton conduction process across six kinds of 2D crystals, namely graphene, h-BN, β12 boron sheet,27 X3 boron sheet,27 phosphorene28 and silicene.29 To clarify the proton conduction mechanism, three proton...
penetration modes: dissociation-penetration, adsorption-penetration, and direct penetration are proposed. The proton penetration energy barriers across the 2D crystals in aqueous environment incorporating explicit water molecules are calculated using the density functional theory (DFT) method. Our work shed light on the proton conduction mechanism across 2D crystals and identified promising candidates for future proton exchange membrane application.

DFT calculations were performed using the ABINIT software package. Perdew–Burke–Ernzerhof (PEB) general gradient approximation (GGA) and projector augmented wave (PAW) pseudopotentials were employed to treat the exchange-correlation functionals and electron–ion interactions. Grimme’s D2 correction was adopted to describe the van der Waals interaction. For geometrical optimization, all the atoms were fully relaxed to reach a force tolerance of 0.01 eV/Å. Proton penetration energy barriers were calculated using the climbing image nudged elastic band (CI-NEB) method. For calculations considering vacuum environment, a 15 Å vacuum gap was added to prevent the interaction between slabs. The cutoff energy was set to be 20 Ha and the k-point mesh was set to be $3 \times 3 \times 2$. Constrained minima hopping algorithm implemented in the Atomic Simulation Environment (ASE) was used to determine the stable H$_2$O and H$_3$O$^+$ adsorption configurations on 2D crystals. For each 2D crystal adsorbed with H$_2$O or H$_3$O$^+$, 20 minima hopping steps were performed,

Figure 1. Geometries and charge density plots of (a) graphene, (b) h-BN, (c) $\beta_{12}$ boron sheet, (d) $\chi_3$ boron sheet, (e) phosphorene, and (f) silicene. The contour line in the charge density plots represents 0.05 e/Bohr$^3$.

Figure 2. Proton conduction across (a) graphene, (b) h-BN, (c) $\beta_{12}$ boron sheet, (d) $\chi_3$ boron sheet, (e) phosphorene, and (f) silicene in a vacuum environment.
and the corresponding geometries of the identified local minima were used to further calculate the adsorption energies. For a neutral system, the adsorption energy was calculated as

\[ E_{\text{ads}} = E_{\text{total}} - E_{\text{substrate}} - E_{\text{adsorbate}} \]  

(1)

where \( E_{\text{total}} \), \( E_{\text{substrate}} \), and \( E_{\text{adsorbate}} \) represent the energy of the total system, the 2D crystal, and the adsorbate. For a charged system, the adsorption energy was calculated as\(^39\)

\[ E_{\text{ads}} = E_a - E_f \]  

(2)

where \( E_a \) is the energy of the system with adsorbate adsorbed on 2D crystals, and \( E_f \) is the energy of the system putting adsorbate far away from 2D crystals.

To prepare the aqueous environment, water molecules were put evenly into the vacuum space to ensure that the density of water in the supercell is close to 1 g/cm\(^3\), which is the experimental value under standard conditions. Then the system went through 50 minima hopping steps to search for the low-lying energy minima in the water configuration space.\(^{40}\) The configuration with the lowest energy was then identified for further calculations. For calculations considering aqueous environment, the cutoff energy was set to be 15 Ha, and the k-point mesh was set to be \( 2 \times 2 \times 1 \). It should be noted that in the calculations on proton conduction in aqueous environment, the calculated energy barriers depend on the water configurations, thus only a qualitative description for the proton conduction process can be provided. In our future work, calculations incorporating the dynamic nature of aqueous environment\(^{23,41–44}\) will be conducted.

The optimized geometries and electron density distribution of considered 2D crystals are shown in Figure 1a–f. To compare the pore size formed by electron clouds, we plot the contour line of 0.05 e/Bohr\(^3\) and define the area enclosed by the first contour line to be the pore size. Graphene and h-BN show the smallest pore size of 0.82 Å, while the \( \beta_{12} \) and \( \chi_1 \) boron sheet show much larger pore size of 1.31 and 1.45 Å. Different from the other cases, the pores formed by the electron clouds of phosphorene and silicene are three-dimensional (3D), as shown in Figure S1. Phosphorene exhibits a puckered structure with a height of 2.12 Å, and silicene exhibits a slightly buckled structure with a height of 0.46 Å. Figure 1e,f show the midplane cross-section of their charge density distribution. The narrowest sizes of the 3D pores are 1.98 Å for phosphorene and 2.74 Å for silicene.

We first calculated the proton penetration energy barriers across 2D crystals in vacuum environment as benchmark. Two penetration routes are considered: the one with both ends fixed 3 Å above the mid of the pores formed by the 2D crystals (path 1); and the one with both ends relaxed to the most stable proton adsorption sites on the 2D crystals (path 2). For path 1, the penetration energy profiles are plotted in blue spheres in Figure 2a–f. Graphene and h-BN exhibit energy barriers of 1.19 and 0.60 eV, respectively, which show good agreement with previous studies.\(^{18,22}\) The \( \beta_{12} \) and \( \chi_1 \) boron sheets show zero proton penetration energy barrier, which are resulted from the electron deficiency of boron atoms. Phosphorene shows an energy barrier as high as 2.95 eV, and the proton penetration route is zigzag instead of straight, which is caused by the complex geometry of its electron density distribution, as shown in Figure S2. For silicene, as the pore size formed by the electron clouds is large and the buckeling is slight, proton can still maintain a direct penetration route and shows a low energy barrier of 0.15 eV. For path 2, Table S1 lists the proton adsorption energy on 2D crystals. All the 2D crystals show strong chemical adsorption toward proton. The proton penetration energy profiles following path 2 are plotted in pink spheres in Figure 2a–f. For most cases, the proton penetration energy barriers of path 2 are much higher than those of path 1. The only exception is phosphorene, where path 2 shows a smoother penetration route and lower penetration energy barrier.

To investigate whether these 2D crystals can effectively block the transportation of other species, we calculated the proton penetration energy barriers of \( \text{H}_3\text{O}^+ \) and \( \text{CH}_3\text{OH} \) across \( \beta_{12} \) boron sheet, \( \chi_1 \) boron sheet and silicene. Since graphene and h-BN show much denser electron distribution and the geometry of phosphorene is too complex, they are unlikely to allow the penetration of \( \text{H}_3\text{O}^+/\text{CH}_3\text{OH} \). For \( \beta_{12} \) and \( \chi_1 \) boron sheets, the \( \text{H}_3\text{O}^+ \) and \( \text{CH}_3\text{OH} \) molecules tend to dissociate as shown in Figure S4–S5 and Figure S9–S10, which is a result of the size-rejection effect, and indicates that these molecules cannot penetrate the 2D boron sheets. For silicene, the energy barriers are 5.85 eV for \( \text{H}_3\text{O}^+ \) (Figure S6–7) and 9.33 eV for \( \text{CH}_3\text{OH} \) (Figure S11–12), indicating that the penetration of \( \text{H}_3\text{O}^+ \) and \( \text{CH}_3\text{OH} \) are highly impossible to occur at room temperature. As the interactions between \( \text{H}_3\text{O}^+/\text{CH}_3\text{OH} \) and the aqueous phase are mainly weak hydrogen bonds, the calculated penetration energy barriers are expected to change little when considering the explicit water molecules. Thus, for all the 2D
crystals considered, effective blockage of H$_3$O$^+$/CH$_3$OH and larger species can be expected. To study the detailed interactions between 2D crystals and the aqueous phase, we first investigated the adsorption behavior of a single H$_2$O/H$_3$O$^+$ molecule on 2D crystals. After 20 constrained minima hopping steps, stable adsorption configurations of H$_2$O and H$_3$O$^+$ on 2D crystals were identified. All the 2D crystals can maintain their atomic structures with a single H$_2$O adsorbed (Figure S14). The adsorption energies of H$_2$O with searched stable configurations on 2D crystals are plotted in Figure 3a, where the absolute value of all the adsorption energies are smaller than 0.25 eV. The distances between the mass center of H$_2$O molecule and 2D crystals are plotted in Figure 3b, where all the distances are larger than 2.3 Å. The calculation results show that the interactions between H$_2$O and 2D crystals are mainly weak van der Waals forces.

The adsorption energies of H$_3$O$^+$ with searched stable configurations on 2D crystals and the distances between H$_3$O$^+$ and 2D crystals are shown in Figure 4a,b, where all the 2D crystals show strong interactions with H$_3$O$^+$ except graphene. When analyzing the geometry of the adsorbed H$_3$O$^+$, the dissociation of H$_3$O$^+$ into a H$_2$O molecule and a proton adsorbed on the 2D crystals was observed for all the 2D crystals except graphene (Figure S15). The H$_3$O$^+$ dissociation can be reflected by the longest O−H bond length (>1.5 Å) (Figure 4c) and the nearest distance between the H atom and the 2D crystals (Figure 4d). For h-BN, β$_{12}$ boron sheet, χ$_5$ boron sheet and silicene, the dissociation of H$_3$O$^+$ is strongly energetically preferred. By contrast, for phosphorene, the energy difference

Figure 4. (a) H$_3$O$^+$ adsorption energies, (b) the distances between H$_3$O$^+$ and 2D crystals, (c) the longest O−H bondlengths of the adsorbed H$_3$O$^+$, and (d) the nearest H to 2D crystal distances of the searched adsorption configurations.

Figure 5. Proposed aqueous proton penetration modes.
between the dissociated H$_3$O$^+$ adsorption configuration and intact H$_2$O$^+$ adsorption configuration is relatively small (<0.25 eV), thus both adsorption configurations appeared in the identified local minima. As H$^+$ shows much stronger adsorption toward the 2D crystals than H$_2$O as listed in Table S1, the H$_3$O$^+$ exhibits much larger adsorption energies than H$_2$O on the considered 2D crystals.

Based on the above findings that H$_3$O$^+$ prefers to dissociate into a H$_2$O molecule and a proton adsorbed on the surface for most 2D crystals considered, we propose three possible proton penetration modes. (i) Dissociation-penetration mode. As shown in Figure 5a, a proton first dissociate from a hydronium ion, penetrate across the 2D crystals and then combine with a water molecule to form another hydronium ion. (ii) Adsorption-penetration mode. As shown in Figure 5b, the proton may prefer to adsorb on the 2D crystals, and then flip over to the other side. (iii) Direct penetration mode. As shown in Figure 5c, this penetration mode involves the direct penetration of a hydronium ion and require large pore size of the 2D crystals. Since the pores of the considered 2D crystals can effectively block H$_3$O$^+$ transportation, the direct penetration mode will not be considered in the present work.

For all the prepared aqueous systems filled with explicit water molecules, a vacuum gap about 3.0 Å between the 2D crystals and the aqueous phase was observed (Table S3), which show good agreement with the weak interaction between 2D crystals and H$_2$O molecule calculated above. Due to the high flexibility of $\beta_{12}/\chi_3$ boron sheets and silicene, structural distortion of the pores in these 2D crystals were observed. For the $\beta_{12}$ boron sheet, a water molecule bonds with a boron atom as shown in Figure S6a, and the boron atom protrudes from the 2D plane, causing the distortion of neighboring pores. For the $\chi_3$ boron sheet, a pair of water molecules self-dissociated into a hydronium ion and a hydroxide ion near the surface. The oxygen atom in the hydronium ion forms a B–O bond with the protruded B atom as shown in Figure 6b, which also induced the distortion of the neighboring pores. Here we define the pores far away from the distorted B atom as “normal pore” and the pores contain the distorted B atom as "distorted pore". In the following, aqueous proton conduction across these two kinds of pores will be discussed separately. For silicene, water self-dissociation was also observed near the surface as shown in Figure S16. Several Si–O bonds with O come from both hydroxide ions and water molecules were formed. Since for silicene, all the pores are distorted to a certain degree in the supercell considered, we will only discuss the proton conduction through the distorted pores. The structural distortion phenomenon is not observed when calculating the adsorption energy of a single H$_2$O molecule on 2D crystals, which emphasizes the importance of incorporating explicit water molecules to study the proton conduction behavior in aqueous environment.

To study the aqueous proton conduction across 2D crystals following our proposed modes, the proton penetration energy barriers across the undistorted pores of graphene, h-BN, $\beta_{12}$ and $\chi_3$ boron sheets, and phosphorene were first calculated. An extra proton was introduced into the system either attached to a water molecule near the 2D crystals or adsorbed on the 2D crystals. The calculated energy barriers are listed in Table 1, and the detailed energy profiles and geometries are provided in Figure S17–S36. We denote the dissociation-penetration mode and the adsorption-penetration mode as “aq1” and “aq2”, respectively. The incorporation of aqueous environment introduces asymmetry in the energy profiles. We distinguish the two penetration energy barriers for a single case with “→” and “←” to represent the reaction direction. For the dissociation-penetration mode, the energy barriers are >4.31 eV for graphene, > 3.55 eV for h-BN, and >2.44 eV for phosphorene. Thus, the dissociation-penetration mode is not feasible for these three 2D crystals at room temperature. By contrast, for the normal pores in the two kinds the boron sheets exhibit much lower energy barriers close to 1.0 eV, making them promising choices for proton exchange membrane application.

Then we considered the proton penetration across the distorted pores in $\beta_{12}$ boron sheet, $\chi_3$ boron sheet, and silicene. For $\chi_3$ boron sheet and silicene, as the self-dissociation of water
molecules occur near the distorted pores, the conduction behavior of the proton in the self-dissociated H$_2$O$^+$ was also studied, and corresponding systems were labeled as the “neutral system”. Accordingly, the systems containing the introduced extra proton were labeled as the “charged system”. The calculated penetration energy barriers are listed in Table 2, and the corresponding energy profiles and geometries can be found in Figure S37–S52. For the $\beta_{12}$ boron sheet, the proton penetration energy barriers through the distorted pores following the dissociation-penetration mode are a bit lower than those through the normal pores, and the penetration energy barriers following the adsorption-penetration mode are much lower (0.063–0.25 eV) than those through the normal pores. For $\chi_3$ boron sheet, the proton penetration energy barriers through the distorted pores following the dissociation-penetration mode are slightly higher than those through the normal pores for both neutral and charged systems. While for the adsorption-penetration mode, the energy barrier can be lowered to 0.55 eV, much lower than those calculated for the normal pores situation. For silicene, the proton penetration energy barriers through the distorted pores are >1.58 eV (neutral system) and >1.15 eV (charged system) following the dissociation-penetration mode, and >1.39 eV following the adsorption-penetration mode.

To qualitatively investigate which penetration mode is more likely to occur, we calculated the transformation energy barrier for a proton in H$_3$O$^+$ mode to adsorption mode near the distorted atoms in $\beta_{12}$ boron sheets and silicene as listed in Table 4.

Table 2. Proton Penetration Energy Barriers in Aqueous Phase Across the Distorted Pores in $\beta_{12}$ Boron Sheet, $\chi_3$ Boron Sheet, and Silicene

<table>
<thead>
<tr>
<th></th>
<th>$\beta_{12}$ boron sheet (distorted pore)</th>
<th>$\chi_3$ boron sheet (distorted pore)</th>
<th>silicene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{b\text{aq1}}$ ($\rightarrow$)/eV (neutral)</td>
<td>--</td>
<td>1.89</td>
<td>2.15</td>
</tr>
<tr>
<td>$E_{b\text{aq2}}$ ($\rightarrow$)/eV (neutral)</td>
<td>--</td>
<td>1.29</td>
<td>1.58</td>
</tr>
<tr>
<td>$E_{b\text{aq1}}$ ($\rightarrow$)/eV (charged)</td>
<td>1.30</td>
<td>1.96</td>
<td>1.62</td>
</tr>
<tr>
<td>$E_{b\text{aq2}}$ ($\rightarrow$)/eV (charged)</td>
<td>1.69</td>
<td>1.53</td>
<td>1.15</td>
</tr>
<tr>
<td>$E_{b\text{aq1}}$ ($\rightarrow$)/eV (charged)</td>
<td>0.25</td>
<td>0.55</td>
<td>2.04</td>
</tr>
<tr>
<td>$E_{b\text{aq2}}$ ($\rightarrow$)/eV (charged)</td>
<td>0.063</td>
<td>1.32</td>
<td>1.39</td>
</tr>
</tbody>
</table>

The detailed energy profiles and geometries can be found in Figure S63–S68. For $\beta_{12}$ and $\chi_3$ boron sheet, the H$_2$O$^+$ mode is preferred for the proton over the adsorption mode near the distorted atoms, and the energy barriers for the transformation process are relatively high. By contrast, for silicene, protons in the adsorption mode show lower energy than protons in the H$_3$O$^+$ mode, and protons in the H$_2$O$^+$ mode can easily transform to the adsorption mode ($E_b = 0.046$ eV). Thus, for proton conduction across the distorted pores of $\beta_{12}$ and $\chi_3$ boron sheets, the dissociation-penetration mode is more likely to occur, while for the proton conduction across silicene, the adsorption-penetration mode is more likely to occur.

In conclusion, we studied the proton conduction behavior across six representative 2D crystals. To clarify the proton conduction mechanism, three penetration modes—dissociation-penetration, adsorption-penetration, and direct penetration—are proposed. Which penetration mode is more likely to occur depends on the detailed interactions among proton, aqueous phase, and 2D crystals. Based on the calculation results, proton penetration across graphene and h-BN are highly impossible at room temperature. The experimentally observed proton conductivity may be attributed to the atomic defects or bias potential. Although it possesses large electron pore size, the puckered structure of phosphorene strongly hinders the penetration of protons. The $\beta_{12}$ boron sheet, $\chi_3$ boron sheet, and silicene exhibit relatively lower proton penetration energy barriers, and can be expected to provide satisfied proton conductivity when serving as proton exchange membranes. Our study provides insight into the proton conduction mechanisms across 2D crystals in aqueous environments, and we identified the $\beta_{12}$ boron sheet, $\chi_3$ boron sheet, and silicene to be promising materials for proton exchange membrane applications.

### ASSOCIATED CONTENT

#### Supporting Information

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Charge density plots of 2D crystals; H$^+$ penetration route across phosphorene; H$^+$ adsorption energies and geometries on 2D crystals; H$^+$ adsorption energies and geometries on 2D crystals; H$_2$O and CH$_3$OH penetration across $\beta_{12}/\chi_3$ boron sheet and silicene; energy profiles and bond length changes of H$_2$O$^+$ and CH$_3$OH penetration across silicene; representative H$_2$O/$\cdot$
H₂O° adsorption geometries on 2D crystals; density of water and the distances between aqueous phase and 2D crystals in the simulation box; geometries of silicene in aqueous environment; energy profiles and geometries of proton penetration across six kinds of 2D crystals following dissociation-penetration and adsorption-penetration modes; energy profiles and geometries for proton transformation from H₂O° form to adsorption form on the surfaces of 2D crystals. (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*Tel.: (852) 2358 8647; E-mail: metzhao@ust.hk (T.S. Zhao).

ORCID
Le Shi: 0000-0003-1468-4549
Ao Xu: 0000-0003-0648-2701
Tianshou Zhao: 0000-0003-4825-2381

Notes
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■ REFERENCES


