Proton Redox and Transport in MXene-Conﬁned Water

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ABSTRACT: The redox reaction of intercalated protons is key to the pseudocapacitance of MXenes (two-dimensional (2D) carbides and nitrides) in H2SO4. However, an atomistic understanding of proton redox and transfer in water conﬁned between MXene layers is still lacking. Here, we use ﬁrst-principles molecular dynamics (FPMD) simulations to reveal the proton-transfer mechanism in MXene-conﬁned water layers of different thicknesses by using O-terminated Ti3C2 as a prototypical MXene. We found that the proton redox process takes place reversibly between surface ~O sites and interfacial water molecules, intermitted by the more frequent in-water proton-transfer events. The surface redox rate is much higher in the highly conﬁned one-layer water than in the two or three layers of water. Proton mobility increases with the water-layer number and already approaches the bulk value in the three-layer water. The proton transfer still follows the Eigen−Zundel−Eigen mechanism in the 2D-like conﬁned water (regardless of the thickness) as in the 3D bulk water via the special pair dance. Our model in the case of two layers of water is in excellent agreement with the experimental interlayer spacing after charging the Ti3C2O2 electrode in H2SO4. Our ﬁnding from FPMD of fast surface redox and in-water transfer for the intercalated protons implies that other processes such as the intercalating step are likely the bottleneck for the ionic transport.

KEYWORDS: MXene, conﬁned water, proton diffusion, surface redox reaction, ﬁrst-principles molecular dynamics

INTRODUCTION

MXenes are a family of two-dimensional (2D) materials, consisting of transition metal carbides, nitrides, and carbonitrides with the general chemical formula of Mx+yXn (M = transition metal; X = C/N). They can be synthesized via the selective removal of the main-group “A” element from the MAX phases by chemical etching in ﬂuorine-containing acidic solutions. MXenes have been used as electrode materials for batteries, supercapacitors, and electrocatalysts. They are also explored for electronics and membrane applications.

Previous studies have shown that MXenes exhibit pseudocapacitance in the H2SO4 electrolyte. The proton-involved surface redox reaction has been found to be the key process to induce the pseudocapacitive behavior of MXene. Computational screening suggested new nitride-based MXenes for higher pseudocapacitance. In aqueous solutions, it was found that the interlayer distance in MXene layers could expand due to the intercalation of water molecules and cations. The intercalated water molecules raise the accessibility of proton to the surface redox reaction sites.

Despite the many recent reports of MXenes for pseudocapacitive energy storage in acidic electrolytes, the mechanism and dynamics of proton transfer in the intercalated water inside MXene layers are not well understood. In particular, one wonders how water under conﬁnement and the water-layer thickness affect the mechanism of proton transfer and how the surface redox process of the proton couples with the proton transport in water in the context of the Grotthuss mechanism. Other important questions include: how can the transport and the system be optimized to enhance redox while not limiting transport? How can the proton-transfer mechanism be tuned by the electrode such as different surface terminations and by the electrolyte such as pH?

To begin to address the important questions above, here, we employ ﬁrst-principles methods to examine the behavior of proton in different scenarios of interaction with a MXene layer to provide a dynamic picture. We chose the prototypical MXene, Ti3C2, for which many experimental studies have

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been published in terms of its pseudocapacitive energy storage in the H₂SO₄ electrolyte. During chemical processing, the surface of Ti₃C₂ will be terminated by groups such as O, OH, or F (minor). In this work, we will focus on the O termination which becomes OH when the MXene layer is reduced in the H₂SO₄ electrolyte. We use first-principles molecular dynamics (FPMD) simulation to examine proton redox and transport in water confined inside Ti₃C₂O₂ layers. Our analysis of the FPMD trajectories focuses on the surface redox chemistry and the diffusion of protons within the hydrogen bond network of confined water layers. Below, we first describe the method details for our FMPD simulations.

■ METHOD

Kohn–Sham density functional theory (KS-DFT) implemented in the Vienna ab initio Simulation Package (VASP) was used for structure optimization and FPMD. The generalized-gradient-approximation in the form of Perdew–Burke–Ernzerhof (PBE) functional was used for electron exchange-correlation in combination with DFT-D3 to account for van der Waals interactions. The electron–nuclei interaction was described by projector augmented wave (PAW) potentials. An energy cutoff of 500 eV was used for the plane-wave basis set. A k-point mesh of 3 × 3 × 1 was used for sampling the Brillouin zone. Convergence criteria were 10⁻⁵ eV in energy and 0.01 eV/Å in force for geometry optimization.

To model the MXene–water (proton)–MXene structure, we used an orthorhombic supercell (a = 10.52 Å; b = 9.11 Å) of the Ti₃C₂O₂ monolayer (12 formula units). Then, three protons and different layers of water (one, two, and three layers corresponding to 10, 17, and 26 water molecules per cell, respectively) were randomly inserted into the cell. The whole simulation cell is charge neutral, so there are extra electrons in the electrode to balance the proton charge in the water layer. The charge for the proton or hydronium ion can be viewed as a charge defect on an oxygen atom in the water layer. Because all of the H atoms are bonded to O atoms in our system, we tracked the charge by monitoring the oxygen atoms with an extra H atom or O−H bond (i.e., O atoms with three bonded H atoms in the water layer). Since about 0.5 H⁺ per formula unit can be stored in MXenes such as Ti₃C₂O₂, our use of three protons in 12 formula units simulates an early stage of the charging process. To determine the optimal interlayer spacing (the c parameter), we calculated the total energy as a function of the interlayer distance (see the next section).

After an optimized interlayer spacing was obtained, FPMD simulations were performed in canonical ensemble (NVT) with Nosé–thermostat at 300 K for 16 ps (with a time step of 1 fs). The system was considered well equilibrated when the temperature stabilized, which was usually achieved after a few picoseconds. From the time-dependent trajectory of O₀ (oxygen atom of the hydronium ion), we can obtain its time-dependent mean square displacement (MSD)

\[
\text{MSD}(\Delta t) = \langle (r(t_0 + \Delta t) - r(t_0))^2 \rangle = \frac{1}{N_t - m} \sum_{k=0}^{N_t-m-1} \langle (r(k + m) - r(k))^2 \rangle
\]

where \( \vec{r} \) represents the position of the particle, \( m \) is the number of snapshots for \( \Delta t \), and \( N_t \) is the total number of snapshots. To evaluate the contribution from different directions, we also decomposed the MSD to xy plane and z direction by projecting the position to the relative direction. The diffusion coefficients were obtained by using the Einstein relation,

\[
D = \frac{1}{6} \frac{\partial \text{MSD}}{\partial \Delta t},
\]

Proton diffusion in bulk water was also

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Figure 1. Optimized structures of protons confined in Ti₃C₂O₂ with different layers of water molecules: (a) one; (b) two; and (c) three layers. Ti, cyan; C, gray; O, red; H, white.
simulated by a cubic unit cell of 12.36 Å in length containing 63 water molecules and one proton.

## RESULTS AND DISCUSSION

The interlayer spacing is a key parameter for water/proton confinement between MXene layers. To further understand the degree of confinement on the proton transfer, the water layer is a key variable that we address here. Below, we first determine the interlayer spacings for the different water layers in confinement.

### Proton and Water Confined in Ti3C2O2 Layers.

Experimental observation showed that the interlayer distance increases with water intercalated between MXene layers.21 Before modeling the proton transport in such a system, we first determine the optimal interlayer spacing as the thickness of the intercalated water is varied. We used an orthorhombic unit cell of the Ti3C2O2 monolayer and added different layers of water with three protons randomly distributed between the two Ti3C2O2 monolayers (Figure 1). Here, we chose the O termination for the MXene because as protons get reduced on the surface, some O-terminal groups will be converted to OH groups. In other words, the O- and OH-terminations are interconvertible under the acidic electrolyte.26

For each different number of the water layer, we optimized the structure as a function of the interlayer distance to determine the interlayer spacing with the lowest energy. As shown in Figure 2, the optimal interlayer spacing is 12.5, 15.0, and 18.0 Å for one, two, and three confined water layers, respectively. We estimated the densities of the confined water and proton. A spline is used to connect the points for each case.

![Relative energy as a function of c lattice parameter of Ti3C2O2 with confined water and proton. A spline is used to connect the points for each case.](image)

Figure 2. Relative energy as a function of c lattice parameter of Ti3C2O2 with confined water and proton. A spline is used to connect the points for each case.

and 18.0 Å for one, two, and three confined water layers, respectively. We estimated the densities of the confined water layers and found them to be close to 1 in the cases of two and three layers (1.02 and 0.99 g cm⁻³, respectively). In the case of the one-layer water, the strong interfacial interaction made the water density greater than 1 (1.15 g cm⁻³). With these optimal interlayer spacings, we next performed FPMD simulations.

### Proton Redox and Transport in Water Confined between Ti3C2O2 Layers.

The mechanism of proton transfer in water has been extensively investigated in the past decades via various spectroscopic techniques and computer simulations. Here, we wonder how proton transfer in confined water is different from that in bulk water. Following the notation from the literature,22 we define the O atom in the hydronium ion as O₀ and its nearest O atom in the first coordination shell as O₁ₓ atom; the O₀–O₁ₓ interaction is called a special pair (Figure 6). In Figure 7 (upper panel), we display the change of identity of O₀ and O₁ₓ during a trajectory of 0.5 ps, which signals proton-transfer events. During the ‘short’ segments, the O₀ identity is short-lived and switches back and forth with the O₁ₓ identity; during the ‘long’ segments, the O₀ identity is long-lived, but the O₁ₓ identity changes among three different O atoms. As a previous study proposed,32 the short segments correspond to the Zundel state in which the O₀ and O₁ₓ atoms share the proton, and the O₀–H and O₁ₓ–H bond lengths are close (Figure 7 lower panel). The ‘long’ segments correspond to the Eigen state of the hydronium ion coordinated by three water molecules in the first coordination shell, and the three O atoms do the so-called ‘special pair dance’, whereby the identity of the O atom closest to O₀ (i.e., O₁ₓ) switches among the three water molecules in the first coordination shell (Figure 6).32

In this case, the O₀–H bond is much shorter than the O₁ₓ–H bond (Figure 7, lower panel). Taken together, Figure 7...
shows that proton transfer follows the same Eigen−Zundel−Eigen mechanism in MXene-confined water as in bulk water. **Proton Diffusivity in Water Confined between Ti$_3$C$_2$O$_2$ Layers.** After revealing the mechanism of proton transfer in the confined water, we next quantify its mobility.

**Figure 3.** Snapshots of typical proton surface redox processes in water confined between Ti$_3$C$_2$O$_2$ layers: (a) one layer; (b) two layers; and (c) three layers of confined water. The interfacial water/H$^+$ involved in the surface redox process and the hydronium ions are highlighted by a ball-and-stick model. Cyan, Ti; gray, C; red, O; white, H.

**Figure 4.** Number of proton surface redox (green) vs in-water proton-transfer (orange) events with time for different layers of water with protons confined between Ti$_3$C$_2$O$_2$ layers.

**Figure 5.** Number of proton surface redox (green) vs in-water proton-transfer (orange) events with time for different layers of water with protons confined between Ti$_3$C$_2$O$_2$ layers.

**Figure 7.** shows that the key to proton transfer is the changing of the O$_0$ identity, namely, the O atom in the hydronium ion (Figure 6). To track the proton motion in the water layer, we therefore computed the MSD of the O$_0$ atoms and further decomposed the MSD into the $xy$ plane and the $z$ direction, as
shown in Figure 8a. One can see that regardless of the number of water layers, the MSD in the z direction is very small compared to the total MSD. In other words, proton mobility is dominated by the movement in the xy plane.

The simulated diffusion coefficients from MSD for protons in the confined water layers are shown in Figure 8b. For comparison, we also simulated proton transport in bulk water (with the same FPMD method) and got 9.09 ± 2.25×10^{-9} m^2 s^{-1}, which is comparable to a previous simulation with the PBE functional33 and the experimental value34 of 9.31×10^{-9} m^2 s^{-1}. The simulated diffusion coefficients for protons in Ti3C2O2-confined water are all lower than the bulk value. In the case of the three layers of water, the simulated value is 5.56×10^{-9} m^2 s^{-1}. This value further decreases to 2.98×10^{-9} m^2 s^{-1} for the two-layer water and 1.59×10^{-9} m^2 s^{-1} for the one-layer water. So proton transport becomes slower as the interaction between the water layer and the MXene surfaces becomes stronger.

Figure 8a shows that proton transfer is 2D-like for the three different thicknesses of the water layer. The interfacial interaction from the confinement plays a more significant role in slowing down the proton transfer in the cases of one layer and two layers of water, where all of the water molecules

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**Figure 5.** Proton surface redox rate constant (a) and the average number of water molecules hydrogen-bonded to the hydronium ion (b) for different layers of water with protons confined in Ti3C2O2 layers.

**Figure 6.** Typical solvation structure of hydronium ion in water. The O atom in the hydronium ion is labeled as O0; the O atoms in the first coordination shell are labeled as O1; the closest labeled as O1x, and the other two labeled as O1y and O1z. The special pair refers to O0 and O1x.

**Figure 7.** Change of O0 and O1x identity (upper panel) and their O–H bond lengths (lower panel) with time during a typical in-water proton-transfer event. The ‘long’ or ‘short’ labels refer to the relative duration of the O0 identity. “Special pair dance” refers to the correlated motion whereby the identity of the O1x around O0 switches among the three water molecules in the first coordination shell of O0 (Figure 6). Oa, Ob, Oc, and Od represent different water oxygen atoms.
are directly interacting with the electrode surfaces. In the case of three layers of water, there is now a water layer not interacting with the two electrode surfaces directly. In this case, although it is still 2D-like, the proton mobility is much higher and approaches that in bulk water (Figure 8b). We expect that the proton transfer will become more 3D-like as the water layer thickness further increases. A simple extrapolation indicates that five layers of water would yield a proton diffusion coefficient about the same as that in the bulk water.

Comparison with the Experiment and Implications from Our Simulations. Recently, Mu et al. investigated the charging mechanism of the Ti$_3$C$_2$Tx electrode in 1 M H$_2$SO$_4$ using in situ X-ray diffraction. They found that the interlayer spacing expands and shrinks during charge and discharge cycles by about 0.5 Å, and, in the charged state, the interlayer spacing (as defined in Figure 1) expands to 14.3 Å. This is very close to the case of the intercalated protons with two layers of water in between Ti$_3$C$_2$O$_2$ layers in our simulations where we found the equilibrium interlayer spacing to be 15.0 Å. So, our simulations indicate that when cycling the Ti$_3$C$_2$Tx electrode in 1 M H$_2$SO$_4$ using in situ X-ray diffraction, the amount of water confined between MXene layers could vary significantly and its diffusivity could be affected greatly. So, it is desirable to examine how the coexistent cations such as alkali ions play a role in the redox and transport behavior of protons in MXene layers. Further exploration is warranted.

CONCLUSIONS

Using first-principles molecular dynamics (FPMD) simulations, we revealed the mechanisms of proton redox at the Ti$_3$C$_2$O$_2$/water interfaces coupled with proton transfer in thin water layers confined between Ti$_3$C$_2$O$_2$ surfaces. We especially focused on the effect of the thickness of the water layer. Close to 20 ps of simulations at room temperature found that the proton redox process happens reversibly between surface -O sites and water molecules at the interfaces. In between proton surface redox events, more frequent in-water proton-transfer events were observed. As the confined water layer becomes thinner and thinner from three layers to one layer, proton surface redox rate increases, especially by a greater extent from two layers to one layer, but the in-water proton-transfer rate decreases. In the much less confined case of three layers of water, the proton mobility already approaches the bulk value. We further revealed that proton transfer still follows the Eigen–Zundel–Eigen mechanism in the 2D-like confined water (regardless of the thickness) as in the 3D bulk water via the special pair dance. Comparison with recent experiments indicates that our models resemble closely the charged state of the Ti$_3$C$_2$O$_2$ electrode in H$_2$SO$_4$ especially in the case of two layers of water. Moreover, our findings suggest that once protons are intercalated into the water layer confined between the Ti$_3$C$_2$T$_x$ layers, both proton surface redox and in-water proton transfer are fast; despite that, proton transfer is slowed down after confinement. Hence, the bottleneck for the charging process could be the intercalating step, namely, how the protons migrate from the bulk electrolyte into the MXene galleries via the edges of the MXene layers. In addition, during our simulations, we fixed the interlayer spacing, since our models simulated a charged state where the protons are already in between MXene layers; to simulate the intercalation process and address the change of interlayer spacing during cycling, one would do a constant-stress simulation under an applied potential to allow the interlayer spacing to vary. We hope to pursue this end in a future study.

It is important to note that water intercalation in MXene layers often depends on the preparation protocol. Moreover, the presence of water molecules in MXene layers has been attributed to the co-intercalation of ions and, depending on the hydrophilicity of the intercalated metal ions, the amount of water confined between MXene layers could vary significantly and its diffusivity could be affected greatly. So, it is desirable to examine how the coexistent cations such as alkali ions play a role in the redox and transport behavior of protons in MXene layers. Further exploration is warranted.

![Figure 8](image-url) Proton diffusion in Ti$_3$C$_2$O$_2$-confined water layers: (a) total and decomposed mean square displacement (MSD) of the O$_0$ atom; (b) proton diffusion coefficients for different numbers of water layers (value in bulk water included for comparison).


