

Review

Proton storage and transfer in aqueous batteries

Runzhi Qin,^{1,2} Mingzheng Zhang,^{1,2} Shunning Li,^{1,*} and Feng Pan^{1,*}¹School of Advanced Materials, Peking University, Shenzhen Graduate School, Shenzhen 518055, People's Republic of China²These authors contributed equally*Correspondence: lisan@pku.edu.cn (S.L.), panfeng@pkusz.edu.cn (F.P.)<https://doi.org/10.1016/j.matt.2025.102165>

PROGRESS AND POTENTIAL Aqueous batteries have emerged as a promising energy-storage technology due to their inherent safety, low cost, and environmental friendliness, making them appealing for security- and cost-sensitive energy-storage applications. While metallic cations, such as Li^+ , Na^+ , and Zn^{2+} , are typically regarded as the charge carriers in the existing aqueous batteries, there is a rising interest in understanding the role of non-metallic charge carriers in battery performance. Insights into the behavior of protons are of special importance due to their general participation in the charge-transport processes at both electrodes and electrolytes. This review provides a comprehensive retrospective of the previous investigation on proton dynamics during electrochemical energy storage, highlighting the importance of hydrogen-bond networks, as well as the concerted proton-transfer modes therein. The underlying mechanisms could serve as a bridge between proton chemistry and the practical design of aqueous batteries.

SUMMARY

Aqueous batteries are promising energy-storage devices due to their high safety, large capacity, and low cost. Recent studies have revealed significant proton involvement in aqueous batteries, even in non-acidic environments, attributed to the unique proton-transfer mode via hydrogen bonds in water. This review summarizes proton storage in solid electrodes and generalizes the impact of proton transfer on aqueous batteries from conceptual insights to practical examples. The specialized storage mode for protons as charge carriers is introduced, and the principles for electrode-material selection are proposed. Then, two distinct proton-transfer mechanisms are discussed, and the strategies to enhance aqueous-battery performance are analyzed. These strategies include reinforcing proton transfer in electrode materials for higher capacity and faster rates and impeding proton transfer in electrolytes and interfaces to reduce side reactions and expand the electrochemical stability window. Contradictions in proton-tuning strategies across different components are illustrated through detailed cases. This review addresses the general phenomena and challenges related to proton storage and transfer in rocking-chair-type aqueous batteries, aiming to inform the future design and utilization of protons in energy-storage systems.

INTRODUCTION

Energy storage and utilization have been integral to human development. The first application of electrical energy, namely voltaic pile, was in the form of an aqueous battery, introduced by Volta in 1800. In the following years, numerous aqueous batteries, such as nickel-cadmium (Ni-Cd),¹ nickel-metal hydride (Ni-MH),² and lead-acid batteries,³ have been successfully developed and commercialized, significantly transforming societal production and lifestyles. Recently, the pinnacle of rechargeable battery technology has been achieved with lithium-ion batteries (LIBs) utilizing non-aqueous electrolytes.⁴ These non-aqueous batteries have surpassed aqueous batteries by higher output voltage and stability in long-term cycles. Never-

theless, some combustion and explosion incidents highlight the safety hazards of LIBs due to their organic solvents, which remain an unresolved issue (Figure 1A). In comparison, the intrinsic non-flammability of aqueous batteries presents a significant advantage. The research into aqueous batteries continues with vigor due to their lower cost, reduced toxicity, and greater safety, especially for safety-sensitive applications such as wearable devices and large-scale energy-storage systems.^{5,6} Building on the success of LIBs, some rocking-chair-type aqueous batteries have been developed, including sodium-ion batteries⁷ and zinc-ion batteries,⁸ offering promising alternatives in the energy-storage landscape.⁹

The aqueous proton battery has been recognized as a promising battery system. Protons, having the same electric charge



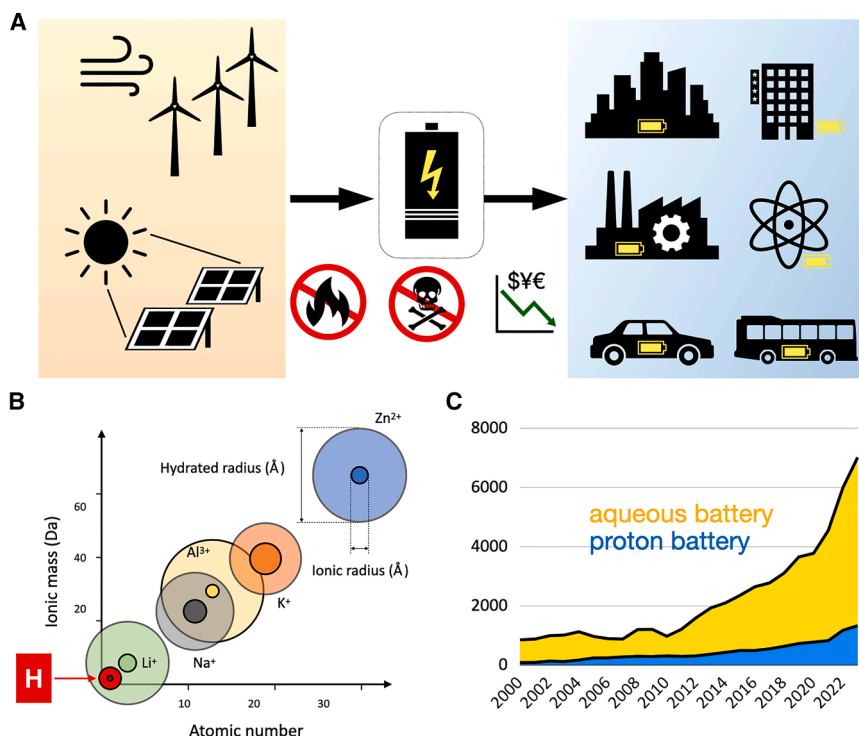


Figure 1. Opportunities and development of proton batteries

(A) Increasing demand for large-scale energy-storage devices with high safety.

(B) Comparison of ionic mass and radius for proton and other charge carriers.¹⁰

(C) Publication trends of aqueous battery and proton battery in the 21st century.

as lithium ions but with a much smaller radius and significantly lower weight, can provide a promising opportunity to deliver higher specific capacities for the cathode materials (Figure 1B). Furthermore, under suitable conditions, proton motion follows a unique mechanism, which is intricately related to hydrogen bonds (H-bonds) and behaves differently from other ions.¹¹ It results in an ultrahigh diffusion rate that is beneficial to the high-rate performance of batteries. As a consequence, proton batteries may present higher capacity and better rate performance than other aqueous candidates. These advantages have motivated researchers to explore proton-based battery systems. Recent studies have also demonstrated that protons and the associated H-bonds play a crucial role in classical aqueous batteries.¹² In some cases, excess protons may result in electrode corrosion and HER, which will deteriorate the stability and efficiency of the battery, while, in others, the participation of protons in charge-discharge cycling may enhance the capacity. The contribution of protons has been somewhat underestimated due to an incomplete understanding of the underlying mechanisms. Therefore, comprehensive understanding and harnessing the potential of protons represent a crucial direction for the future development of advanced aqueous batteries.

In recent decades, advancements in computational methods and detection techniques have progressed dramatically, providing opportunities to delve deeper into the study of protons' behaviors.¹³ For instance, it took nearly a century to visualize H-bonds after the concept was first proposed.¹⁴ Just 9 years afterward, scientists can manipulate H-bonds between water molecules and clearly identify the transformation of different hydroniums.¹⁵ Additionally, emerging clues have indicated the

involvement of H-bonds and protons in aqueous batteries. We are currently benefiting from technological dividends and market incentives, making it an opportune time to realize the potential of proton-based batteries (Figure 1C). However, the behavior of protons in aqueous batteries is complex, which arises from the flexibility of proton-transfer mechanisms and the diversity of H-bond structures in all battery components.¹⁶ The nearly energy-free Grotthuss-type proton motion can sometimes improve the capacity and durability of batteries, but may on the other hand deteriorate the performance if it is not properly designed.¹⁷ Given the lack of a comprehensive

review on H-bonds and proton motion in aqueous-battery systems, this work aims to fill that gap and provide a thorough understanding of these phenomena in the context of aqueous batteries. It should be noted that, here, we focus on LIB-like battery systems featuring insertion/extraction mechanism with inorganic electrode materials rather than systems that convert protons into hydrogen gas and metal hydrides. To the best of our knowledge, such LIB-like systems characterize simpler physicochemical models, higher conversion efficiencies, and better compatibility with existing LIB manufacturing processes. Therefore, in this paper, we regard proton reduction as an unfavorable factor, although this phenomenon may be essential for other battery systems.

This review summarizes the key issues of proton storage and transport in aqueous batteries. We first analyze the difference between protons and other ions as charge carriers and intercalated ions and put forward the design principle for proton-storage materials. Next, we introduce the structure of H-bonds and water, which are important to the analysis of the proton's behavior, and describe in detail two types of proton motion—the Grotthuss mechanism and the vehicle mechanism—to provide intuitive insights. We then discuss the influence of H-bonds and proton motion on various components of the battery, including the electrode, electrolyte, and their interfaces, using specific case studies. Our goal is to present a comprehensive overview of how proton manipulation affects the capacity, rate performance, and durability of aqueous batteries. Finally, we offer perspectives on the performance optimization of future aqueous batteries. This review aims to inspire a deeper understanding of protons and to serve as a design guideline for advanced aqueous batteries.

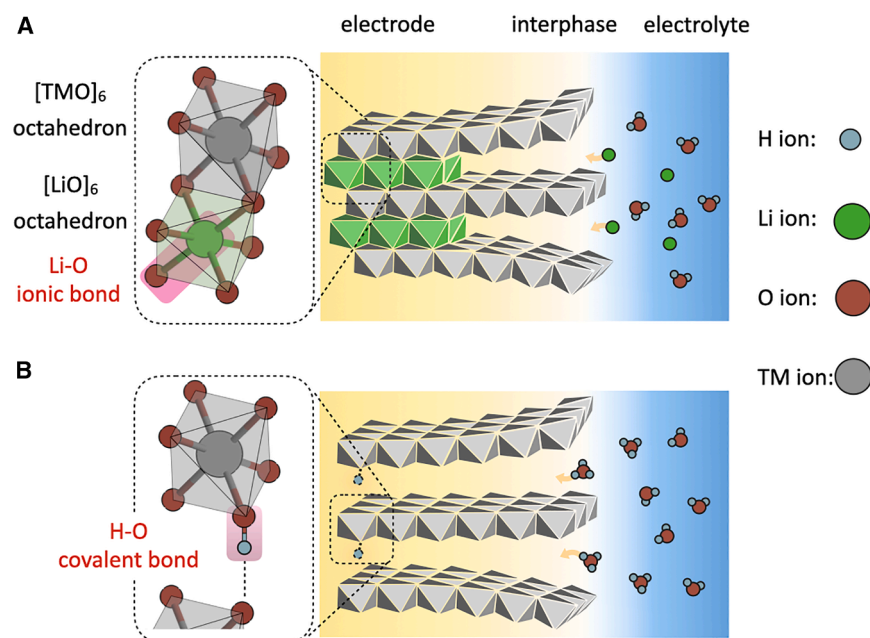


Figure 2. Comparison of bonding property between protons and other charge carriers

(A) Classical layered material with TM-O ionic bond in structure, and lithium ion can form Li-O ionic bond in Li-O polyhedron.

(B) Similar layered material with TM-O ionic bond for proton battery, but protons can only form covalent bond with O, incapable of building a polyhedron.

Further protonation would induce catastrophic consequences because the H-O bonds for the O element can be saturated by excess protons. In some circumstances, over-protonation weakens the transition metal (TM)-O bond, leading to the detachment of TM and O ions and the collapse of the original structure. This phenomenon can be considered as the corrosion of the oxides, especially in low-pH environments or discharged state. For instance, classical cathode materials in LIBs experience structural distortion and capacity fading when protons are intercalated instead of Li ions. Given the fact that most proton batteries are designed in acid electrolyte with high proton concentrations, the electrode materials become more prone to corrosion and capacity fading after cycling. In addition, the acidic environment may also corrode and disintegrate the metallic current collector as well as other accessories, which complicates the battery design.

PROTON BONDING MECHANISMS AND TRANSPORT MODES

Protons and the corresponding bonding properties

A proton, in other words, a hydrogen atom stripped of its electron, has the smallest radius and lightest weight among all ions (Figure 1B). It is one of the simplest systems in physics. Researchers aim to exploit its small and light characteristics to develop proton batteries in a manner similar to LIBs. However, the storage behavior of protons differs significantly from that of traditional metal cations. The most notable difference is the way protons bond with other elements. The proton storage involves intercalation into the solid active material and the formation of chemical bonds with negative ions in the crystal framework, typically oxygen (O) in most cases. The H-O bond is more covalent compared to bonds between O and other charge carriers, such as Li-O and Na-O, which are more ionic.^{18,19} Such H-O covalent bonds correspond to the saturation character of H element, which means that one proton can only form a single strong chemical bond with one O ion. The H-bond may also be formed but it is much weaker, as discussed in the next section. This precludes the formation of a consecutive and robust structure between protons and O ions. Therefore, protons cannot act as pillar ions to reinforce the crystal structural stability, unlike the behavior of Li ions in layered cathodes (Figure 2A; note that the ionic radii are not precisely accurate in these schematic diagrams).²⁰ Protons will hang on the O ions, typically serving as interstitials (Figure 2B). Moreover, the position of bonded protons is not rigidly fixed, in sharp contrast with the situation for other charge carriers, such as the [LiO₆] octahedron. The coordination of protons is quite flexible being affected by the local chemical environment. In most literature, the direction of the bond is neglected and the H-O- structure is generally considered as the hydroxy ion.

Water, H-bonds, and protons

The most prominent characteristic of aqueous batteries is, of course, the presence of water. Water exists not only in the liquid electrolyte but also in some of the solid electrode materials. The influence of water on battery performance is largely achieved through proton transfer and intercalation. On one hand, as a textbook-level reaction, water can ionize into protons and hydroxide ions, thus serving as a source of protons. On the other hand, proton transfer occurs via an efficient mechanism facilitated by the H-bonds in water. Therefore, the H-bonds and their topological networks are crucial for proton regulation.¹⁰

H-bond is a well-established intermolecular force characterized by a weak attraction between a hydrogen atom (H) and a highly electronegative atom possessing a lone pair of electrons (Figure 3A). The electronegative atom covalently bonded to the hydrogen atom acts as a proton donor, typically nitrogen (N), oxygen (O), or fluorine (F). The lone pair-bearing atom, on the other hand, functions as a proton acceptor. This interaction is often depicted as D-H...A, where D/A represents the proton donor/acceptor atom, H signifies the hydrogen atom, and the dotted line (...) indicates the H-bond. The study of H-bonds has a rich history, dating back to the 1920s with the identification of weak bonds in water. Since then, extensive research has been conducted across various scientific disciplines, including physics, chemistry, and biology, to elucidate the role of the H-bond and its associated phenomena. Notably, H-bond is not restricted

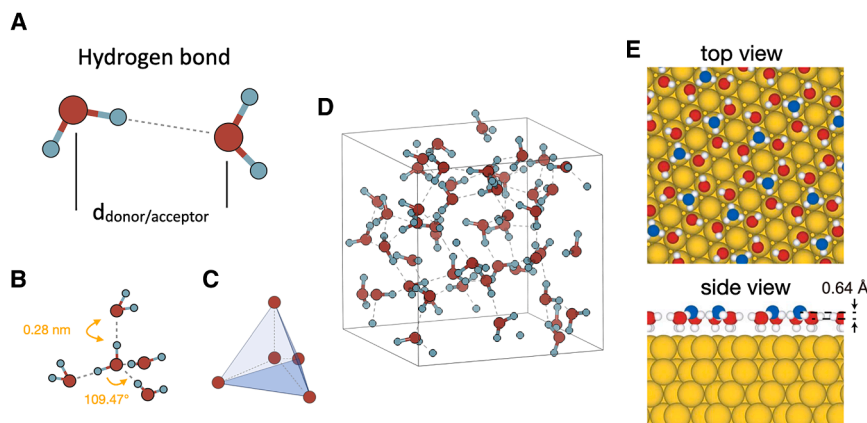


Figure 3. H-bond and water structures

(A) Schematic diagram of H-bond.¹⁰

(B and C) Typical water structures: one water molecule is linked by four other molecules to form a tetrahedron (approximately).

(D) Molecular dynamic result of typical arrangement of 50 water molecules, which exhibits complex and dynamic H-bond networks.

(E) Schematic structures of the Eigen-water monolayer derived from qPlus-atomic force microscopy (AFM) results.¹⁵

to a specific phase; it exists in solids, liquids, and even gases. Examples include proteins, water (H_2O), and hydrogen fluoride (HF) gas. The iconic double-stranded DNA structure is primarily stabilized by a network of H-bonds. The recognition of H-bond's ubiquity stems from two key factors: the inherent tendency of protons to attract electrons and the widespread presence of the $\text{D-H}\cdots\text{A}$ arrangement in nature. This fundamental interaction plays a critical role in various chemical and biological processes, solidifying its status as a universal principle.

The strength of an H-bond serves as a quantitative measure of the attractive interaction. This value significantly influences the physical and chemical properties of a material, as well as the behavior of associated electrochemical reactions. Traditionally, during the time of Pauling, H-bond was primarily considered an electrostatic interaction, stronger than van der Waals forces but significantly weaker than covalent bonds. Recent research, however, suggests that extremely strong H-bonds can almost reach the strength of covalent bonds, implying a more intricate atomic-level mechanism. Generally, H-bond strength ranges from less than 1 kcal/mol to over 40 kcal/mol, depending on the electronegativity of both the donor and acceptor atoms. Weaker H-bonds are typically observed when the proton donor and acceptor exhibit lower electronegativity, such as C-H and P-H bonds acting as donors and π bonds functioning as acceptors. In these cases, the length of the H-bond (i.e., the D-A distance d_{DA}) is typically greater than a specific value. Moderate H-bonds usually have a d_{DA} exceeding 2.7 Å and often involve a covalent D-H bond. Strong H-bonds, conversely, are characterized by shorter d_{DA} distances. These can be identified by a red shift in the characteristic vibrational frequencies for the covalent D-H bond (typically around $3,000\text{ cm}^{-1}$ at room temperature). Short H-bonds (SHBs) can induce a super-harmonic motion of the protons, enabling their near-barrierless transfer. Our research group has proposed a model for SHBs within ionic covalent organic framework membranes (iCOFs) functionalized with $-\text{SO}_3\text{H}$ groups. By manipulating the density of these sulfonate groups on the iCOF's hexagonal unit, diverse H-bond networks can be constructed.²¹ It was demonstrated that reducing the H-bond distance to 2.5 Å can achieve an ultrahigh proton conductivity of $1,389\text{ mS cm}^{-1}$.

Early investigations into H-bonds heavily focused on aqueous systems. The ubiquity of water as a solvent and its intriguing

structure have made it a classical scientific question. Indeed, H-bonds play a critical role in shaping the unique properties of water.²² A water molecule boasts a tetrahedral geometry. The central O atom forms two σ bonds with the s orbitals of H atoms at the apices, utilizing sp^3 hybrid orbitals (Figures 3B and 3C). The remaining two apices house lone pairs of electrons on the O atom. Due to the directional and saturated nature of these interactions, two water molecules can connect via a single H-bond with a defined configuration. In larger water assemblies, the H-bond organization becomes more complex.²³ Advanced calculations and experiments have proved that a single water molecule can form four H-bonds with neighboring water molecules in a tetrahedral arrangement. These four water molecules, in turn, can participate in additional H-bonds with other water or solute molecules. This intricate network of H-bonds effectively connects water molecules into a three-dimensional (3D) network or, more precisely, a collection of interconnected networks (Figure 3D). However, this model is most applicable to bulk ice Ih at 0°C .²⁴ Liquid water, in reality, exhibits a coordination number less than 4, indicating a more dynamic and intricate structure compared to the idealized model.

The precise determination of the structure of water remains a significant challenge, even featuring as one of the 125 Grand Challenges in Science.²⁵ Despite this ongoing pursuit, a picture emerges where water exists as a collection of clusters, with water molecules interconnected by H-bonds of varying strengths.¹⁵ These intermolecular networks are neither too strong (which would result in a rigid, solid-like structure) nor too weak (which would lead to a gaseous state). This unique characteristic of moderate H-bond strength is responsible for the existing form of water as a liquid across a broad temperature range (0°C – 100°C), a characteristic essential for the aqueous electrolytes with surface water adsorption (Figure 3E). In contrast, intramolecular H-bonds generally lower the melting and boiling points of materials. In the context of aqueous electrolytes, H-bond significantly influences several key parameters, including solute solubility, the operational temperature window, and cation mobility, all of which are critical for the performance of aqueous batteries.

Proton transfer in Grothuss model

Protons are distinct from other cations due to their dual nature. They can both participate as a constituent of H-bonds and simultaneously be liberated as free ions by a solute.²⁶ Early

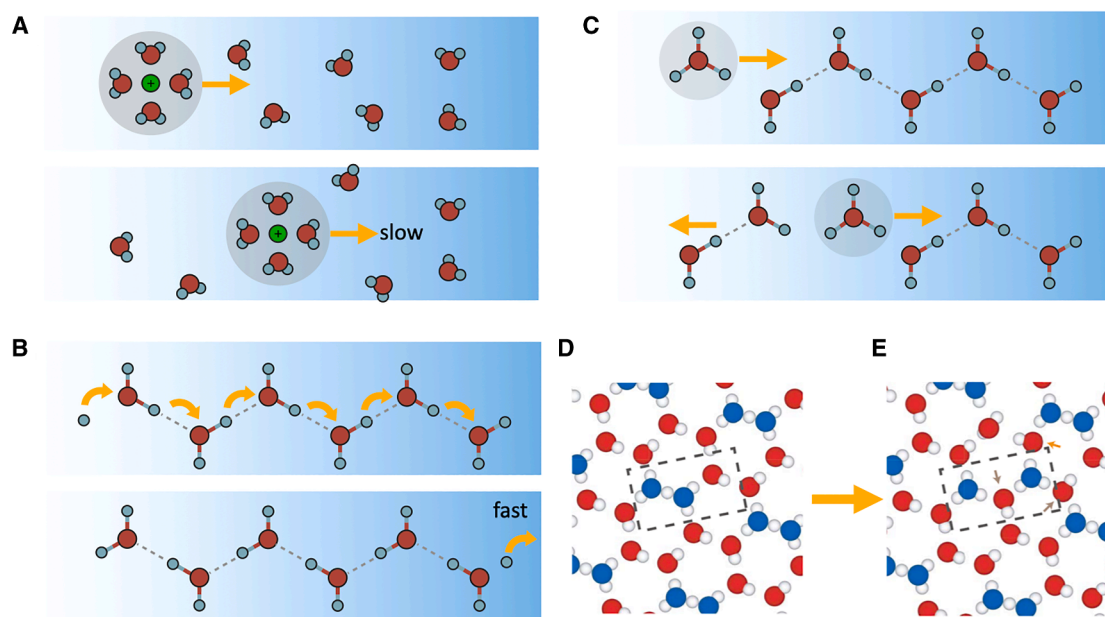


Figure 4. H-bond and water structures

(A) Schematic diagram of common cation transfer.

(B) Schematic diagram of proton transfer via Grotthuss model.

(C) Schematic diagram of proton transfer via vehicle model.

(D and E) Interconversion between the Zundel-type and Eigen-type cations.¹⁵

experiments revealed anomalously high proton mobility, defying traditional cation-movement models (Figure 4A). In 1806, Theodor von Grotthuss proposed a groundbreaking theory explaining this behavior: the Grotthuss mechanism of proton transport.²⁷ This mechanism suggests that protons can migrate between water molecules connected by H-bonds without substantial movement of the entire molecules themselves. A proton (H⁺) typically coordinates with a water molecule to form a hydronium ion (H₃O⁺ or H⁺–OH₂).²⁸ This hydronium ion then forms an H-bond with another water molecule, creating a species like [H⁺–OH₂...OH₂]. During this process, the covalent bond between the first oxygen atom and a favorably positioned hydrogen atom breaks (Figure 4B). Simultaneously, the second water molecule accepts the liberated proton and forms a new H-bond with the first water molecule, represented as [H₂O...HOH₂⁺]. Crucially, while the location of the original proton remains nearly unchanged, the positive charge is transferred from one position to another. This "hopping" motion of the proton along a chain of water molecules, facilitated by the breaking and reforming of H-bonds, is energetically favorable compared to the bulky movement of larger cations through water. The Grotthuss mechanism elegantly explains the exceptional mobility observed for protons in aqueous solutions.

The experimental characterization of protons and H-bonds poses significant challenges due to the fundamental physical properties of protons as the lightest nuclei with the smallest atomic radius. Researchers typically employ vibrational spectroscopy and nuclear magnetic resonance techniques to investigate H-bonding configurations and protonic environments. Moreover, advancements in theoretical calculations

have intensified research on the structure of solvated protons and the timescales and distances involved in their hopping motion. It is now understood that the solvated proton is coordinated with water molecules in more complex structures than previously envisioned. The primary constituents of the solvated proton in aqueous solutions are the Eigen cation (H₃O₄⁺) and the Zundel cation (H₅O₂⁺).²⁸ Very recently, a breakthrough has been achieved by directly visualizing Eigen and Zundel cations for the first time.¹⁵ Using atomic force microscopy, the two types of hydronium ions and their 3D configurations were distinguished clearly by analyzing slices at various depths. Furthermore, the research observed a dynamic interconversion between these two types of cations (Figures 4D and 4E) through the addition or removal of protons via H-bonds,²⁹ which aligns with the observed fast motion of protons in water. Such dynamic construction and deconstruction of the long-range H-bond network plays a crucial role in the Grotthuss mechanism, particularly for electrodes designed to release large amounts of proton-related capacity. Nevertheless, direct observation of the precise site of proton remains beyond the current technological frontier. Some indirect methods, such as predicting proton pathways by monitoring subtle structural variation of bulk material, have emerged as the prevailing experimental paradigm.

Proton transfer in the vehicle model

For a considerable period, the Grotthuss mechanism reigned supreme as the sole explanation for proton motion in electrolytes. In 1982, K.D. Kreuer proposed the new model of proton transfer: the vehicle model.³⁰ This model introduces the concept of "proton carriers" acting as "vehicles" for proton transport. Protons,

akin to "passengers," are envisioned to move as part of hydronium ions (H_3O^+) or ammonium ions (NH_4^+) within these carriers (Figure 4C). Concomitantly, "empty vehicles" (H_2O or NH_3) migrate in the opposite direction. The vehicle model stands in stark contrast to the Grotthuss mechanism. Unlike the latter, which necessitates the breaking and reforming of H-bonds, the vehicle model proposes a process that maintains the integrity of the H-bond network. Furthermore, it deviates from classical Brownian motion, which describes random and independent molecular diffusion. The vehicle model emphasizes the crucial role of the counter-movement of empty vehicles. This key concept has led to the derivation of the Nernst-Einstein equation, which links carrier translational diffusion to proton conductivity. This connection effectively explains the temperature dependence of proton diffusion and the observation that most good proton conductors also exhibit high ion exchange capacity. In recent years, researchers have identified vehicle-type proton motion in diverse systems. The model mainly concerns the situation where a continuous H-bond network cannot be generated. For example, it is believed that long-distance proton transfer in some proton-exchange membranes follows vehicle mode at low-humidity condition and Grotthuss mode at high-humidity condition.³¹ This broader theoretical framework has not only provided more reasonable explanations for previously puzzling experimental observations but has also fostered the design of novel reaction systems based on this mechanism.

PROTON STORAGE IN ELECTRODES

Proton storage in full-proton batteries

One of the goals of utilizing protons as charge carriers is to enhance the specific capacity of electrode materials. Since protons have the lowest weight among all ions, theoretically, the active material storing protons has a mass advantage over those storing other ions. Topologically, the protons can be stored at the empty tetrahedral sites surrounded by the crystal O atoms or the quasi-tetrahedral sites of the O atoms in the form of lattice water (or N in pre-intercalated NH_3). Both the storage sites call for further requirements to crystal structure of the electrode materials. For the first condition, given the fact that the H–O bond is short in length (~ 95.3 p.m.), the possible location is prone to repulsion against the adjacent cations that are also coordinated with this O. Therefore, the position that is the only one left empty for the target O (it means that when this position is occupied, the O atom cannot accommodate other protons) is thermodynamically unfavorable for proton storage. A preferable location is the O at the exposing edges of the TM octahedron, where the O atoms are not fully coordinated, thus leaving space for proton bonding. This situation is often observed in layered or tunnel-like crystals, which expose more sites where crystal symmetry is not satisfied, resulting in more suitable O atoms to accommodate the protons. In the second scenario, lattice water is also commonly found in layered or tunnel-like crystal structures, as these structures have larger spaces to accommodate water molecules. It is also necessary to consider the volume expansion that occurs when protons bind to the O atoms in water molecules. Overall, protons tend to bind with less-coordinated oxygen atoms. Additionally, a hidden assumption is that the inser-

tion and extraction of charge carriers should not significantly affect the crystal structure of the electrode material. Given that protons themselves cannot act as pillars to stabilize the structure (Figure 2B), layered and tunnel-like materials with lower symmetry and larger gaps are favorable for proton storage.³²

However, the high reactivity of protons limits the application of traditional cathode and anode materials as well as the selection of new materials. Considering the potential limitations imposed by water decomposition, the range of suitable TM elements and redox potentials is further narrowed. Figure 5A lists the common cathode and anode materials for full-proton batteries. It can be observed that the most widely used layered oxides, such as Ni-, Co-, and Mn-based oxides, are not included. Although these materials theoretically exhibit good electrochemical performance, their stability and durability in practical applications still require further validation and improvement.³³ Instead, the stable oxides of Mo, Ru, and W have been developed to avoid fast fading in acidic electrolytes.³⁴ However, even these materials in the candidate list are subject to corrosion over long-term cycles,³⁵ which impedes the practical application of proton batteries. Besides, the material availability and cost must also be considered in material selection and battery design. Therefore, it is clear that these oxides mentioned above do not meet the requirements for large-scale commercial use. A deeper understanding of the interaction mechanisms between protons and electrode materials, as well as the development of innovative materials that can remain stable in the presence of protons, remains one of the key challenges in current battery-materials research.

Proton storage in other aqueous batteries

In the early studies of aqueous metal-ion batteries, researchers primarily focused on the insertion/extraction of metal ions such as Li ions and Zn ions, without recognizing the role of protons.⁵ Then, with the advancement of measurement techniques, it has been discovered that protons contribute significantly to the capacity of some aqueous batteries that were not originally designed for proton storage (Figure 5B). Protons are unintentionally introduced into the electrolytes, a process that is inevitable in aqueous solutions due to the dissociation of water molecules. These protons compete with the intended charge carriers, and, in some cases, they may partially supplant other charge carriers due to their smaller radius and faster diffusion kinetics. This competition is influenced by various parameters, including pH value, concentration, and the type of other ions present.³⁶

A typical example is vanadium oxides. V_2O_5 is a classical layered-structure material with a large interlayer spacing of approximately $4.37 \text{ \AA}$, which is advantageous for cation storage.³⁶ Though it is employed as the cathode material for aqueous Al-ion batteries, it has been observed to permit only proton intercalation rather than Al ions (Figure 6A). Researchers proved that the maximum capacity is 1.43 protons per V_2O_5 molecule in $2 \text{ mol kg}^{-1} \text{ Al(OTF)}_3$ electrolyte, and further insertion would alter the V–O bond length and interlayer spacing, leading to structural instability. Then our group experimentally verified that, after pre-intercalating some water molecules, 1.59 protons can be taken up in each unit without apparent structural damage.³⁷ These water molecules not only act as pillars within the

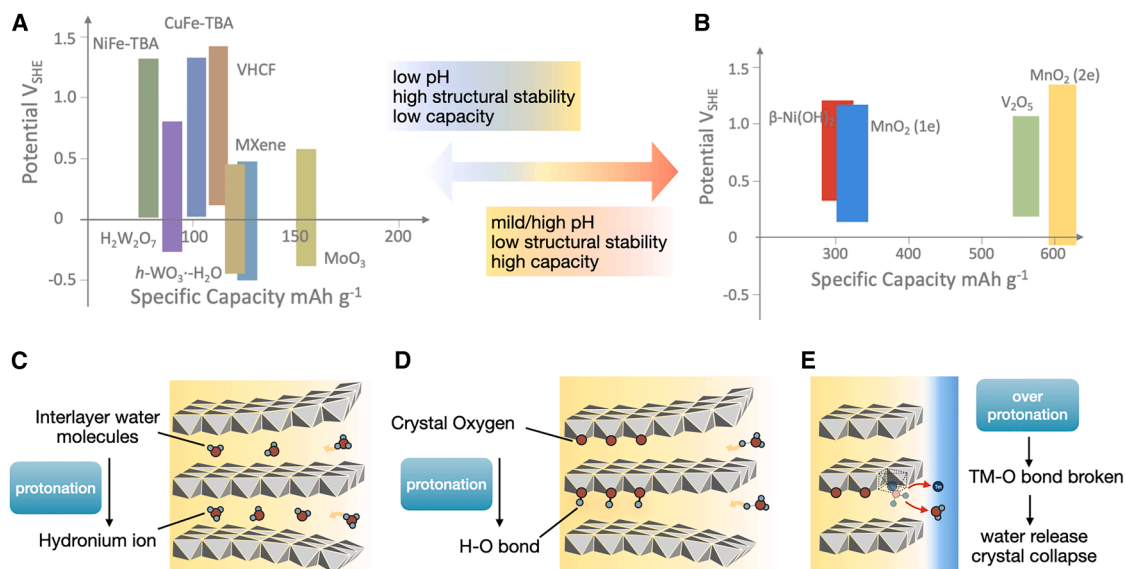


Figure 5. Proton storage in electrode materials

(A) Typical materials for full-proton batteries, which mainly work in low-pH electrolytes and possess limited capacities.³⁴

(B) Typical materials for other aqueous batteries working in mild or high-pH electrolytes, which also have the capability of proton storage.³³

(C and D) Schematic diagram of proton-storage sites in typical crystals: bonding to interlayer water and/or crystal oxygen.

(E) Schematic diagram of crystal collapse and water release with over-protonation.

crystal structure but also enhance proton transfer. As a consequence, the modified material, namely $\text{H}_{0.642}\text{V}_2\text{O}_5 \cdot 0.143\text{H}_2\text{O}$ (Figure 6B), presents high capacity of approximately 245 mAh g^{-1} with negligible capacity loss over 500 cycles in 3 M ZnSO_4 electrolyte, whereas pristine V_2O_5 quickly loses activity within 200 cycles.^{38,39}

A similar phenomenon can be observed in manganese oxide cathodes in aqueous Zn-ion batteries (ZIBs).⁴⁰ In 2011, MnO_2 was proposed in ZIBs, and it was believed that Zn ions are the sole charge carriers for this material.⁴¹ The valence change of the Mn element between +3 and +4 provides a high theoretical specific capacity of 308 mAh g^{-1} , making MnO_2 a promising cathode material.^{42,43} The contribution of protons has gradually been recognized. Our group has discovered that different phases of MnO_2 could exhibit the capability of proton uptake.^{44–46} The contribution of protons can be verified by two pairs of redox peaks in CV profiles, as well as transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) characterization of the byproducts such as $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot n\text{H}_2\text{O}$.⁴⁶ Moreover, the synergistic effect of proton storage and Zn-ion storage was also discovered. These MnO_2 polymorphs cannot deliver enough capacity in either proton-free electrolytes or Zn-ion-free electrolytes. Only in dual-ion electrolytes can they release near-theoretical capacity. Furthermore, a recent study focusing on the classical $\alpha\text{-MnO}_2$ polymorph provides direct evidence for proton storage.⁴⁰ As shown in Figure 6C, $\alpha\text{-MnO}_2$ possesses two distinct tunnel structures, $[2 \times 2]$ and $[1 \times 1]$. Computational analysis and high-resolution TEM results suggested that protons readily bond with lattice O ions located within these tunnels, forming O–H bonds with a characteristic length of approximately 0.10 nm. In contrast, the

larger size and higher charge density of Zn ions make their intercalation less favorable. Indeed, no Zn atom was detected in the discharged sample, challenging the long-held viewpoint of Zn-ion intercalation (Figure 6D). Based on these findings, a logical conclusion can be drawn: optimizing $\alpha\text{-MnO}_2$ for faster proton diffusion holds immense promise for enhancing its performance in energy-storage applications. Future research efforts should focus on strategies to facilitate proton transport within the tunnel structures of materials.

These V- and Mn-based examples inspire us to consider a broader range of materials,³⁸ provided the goal is not restricted to all-proton batteries.⁴⁷ Traditional electrode materials may be capable of storing a significant number of protons in conjunction with other charge carriers. These materials also offer numerous advantages, such as low cost, good environmental adaptability, and well-established production processes. Figure 5B lists some promising material candidates and their redox potentials. We anticipate that these materials hold significant promise for commercial applications in proton storage. An additional benefit lies in the electrolyte selection, because these materials are suitable for mild acidity. Protons can originate from water autoionization, which further reduces the electrolyte cost. However, the precise mechanism of proton intercalation is obscure, and the competition and/or synergistic effects of protons on other ions require further investigation.

PROTON TRANSFER IN SOLID ELECTRODES

Proton transfer via water-based H-bond networks

The exceptional diffusion kinetics of protons make them highly attractive candidates for rechargeable battery applications.

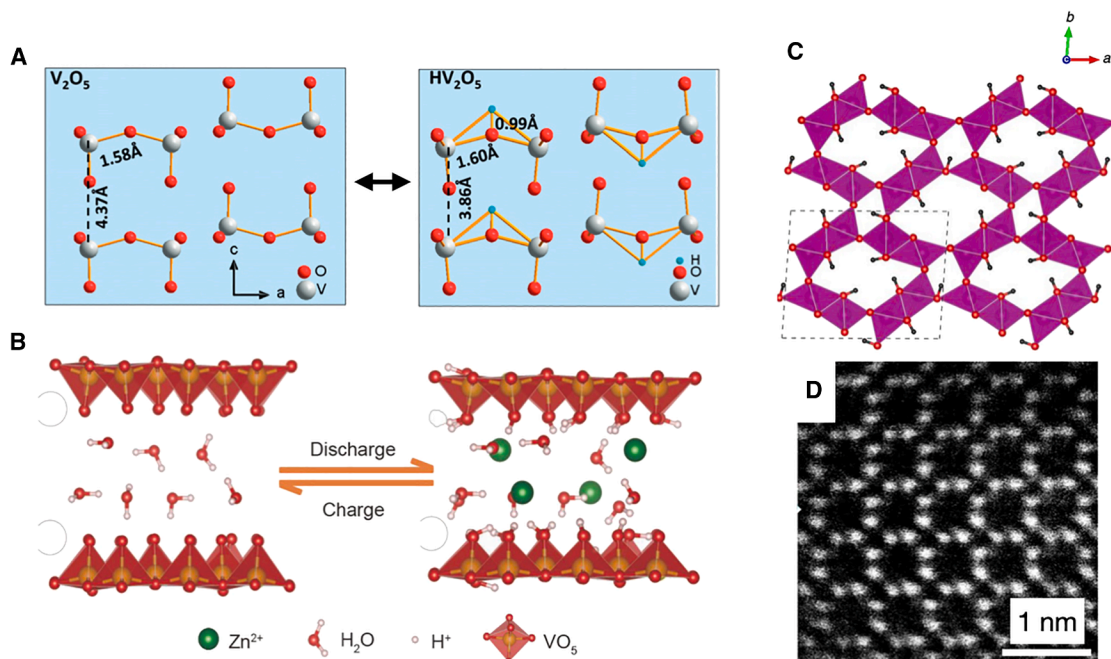


Figure 6. Proton storage in other aqueous batteries

(A) Proton-storage sites in V_2O_5 structure.³⁶

(B) Synergistic storage of proton and zinc ions in $H_{0.642}V_2O_5$ in aqueous zinc-ion electrolyte.³⁷

(C) Theoretical result of proton-storage sites in α - MnO_2 ; the $[2 \times 2]$ and $[1 \times 1]$ tunnels expose sufficient crystal oxygen sites.

(D) TEM result verifies the absence of zinc ions and potassium ions in α - MnO_2 .⁴⁰

Proton batteries offer the potential for exceptional rate capability and high capacity. The Grotthuss mechanism, which governs proton transport through a network of H-bonds, facilitates rapid intercalation/deintercalation kinetics within battery electrodes, surpassing the performance of many other mobile ions. A straightforward approach to leverage the Grotthuss mechanism involves incorporating water-containing H-bond networks into solid-state electrode materials. Several promising materials have been designed based on this strategy, including Prussian blue analogs (PBAs) and WO_3 . These materials aim to exploit the Grotthuss mechanism to achieve high-rate proton-battery performance.

PBAs

PBAs represent a promising class of porous inorganic solid materials for battery applications.⁴⁸ Their abundant and stable structural vacancies endow them with exceptional properties, including gas/ion storage, proton conduction, magnetism, electrical conductivity, and optical functionality. A particularly attractive feature of PBAs for proton batteries is the potential for enhanced Grotthuss conduction through strategic defect engineering.

The most important function for PBAs is the capability of reversible mass transport, which is tightly controlled by the structural vacancies.⁴⁹ One such approach involves tailoring the ligand vacancies within the PBA structure. A recent report describes the design of a CuFe-TBA material, where a reduction in the amount of ferrocyanide ligand vacancies creates interconnected channels between cages.¹¹ These vacancies are charge

compensated by the removal of ferrocyanide and ferrocyanide vacancies, creating a network within the PBA framework (Figures 7A and 7B). Crucially, zeolitic water molecules within the cages can form H-bonds with coordinated water molecules residing in the vacancies (Figure 7C). This interaction fosters the formation of water-molecule chains that bridge these interconnected vacancies. As the vacancy fraction increases to $1/4$, such H-bond chains can be connected with each other.⁵⁰ Computational modeling confirms that proton motion in this material adheres to the Grotthuss mechanism, with protons migrating along the water chains via a pattern of alternating ligand water and zeolitic water ($O1-O2-O1'-O2'$, as depicted in Figures 7D–7F). This arrangement provides the essential water-based H-bond network required for efficient Grotthuss conduction. The engineered CuFe-TBA electrode exhibits exceptional proton-transport characteristics. In full battery with 2 M H_2SO_4 electrolyte, the material delivers a high capacity of 49 mAh g^{-1} (half of its 1 C rate capacity of 95 mAh g^{-1}) at an extraordinary rate of 4,000 C (380 A g^{-1} , 508 mA cm^{-2}). Remarkably, the CuFe-TBA electrode retains 60% of its capacity even after 0.73 million cycles at 500 C, surpassing the cycle life previously reported for Faraday electrodes. This achievement underscores the potential of materials designed to exploit Grotthuss-type proton motion for high-performance batteries.

Building upon this concept, researchers have explored alternative PBAs with even higher capacities. Another study describes the development of hydrous vanadium hexacyanoferrates (VHCFs) capable of delivering a specific capacity of 108

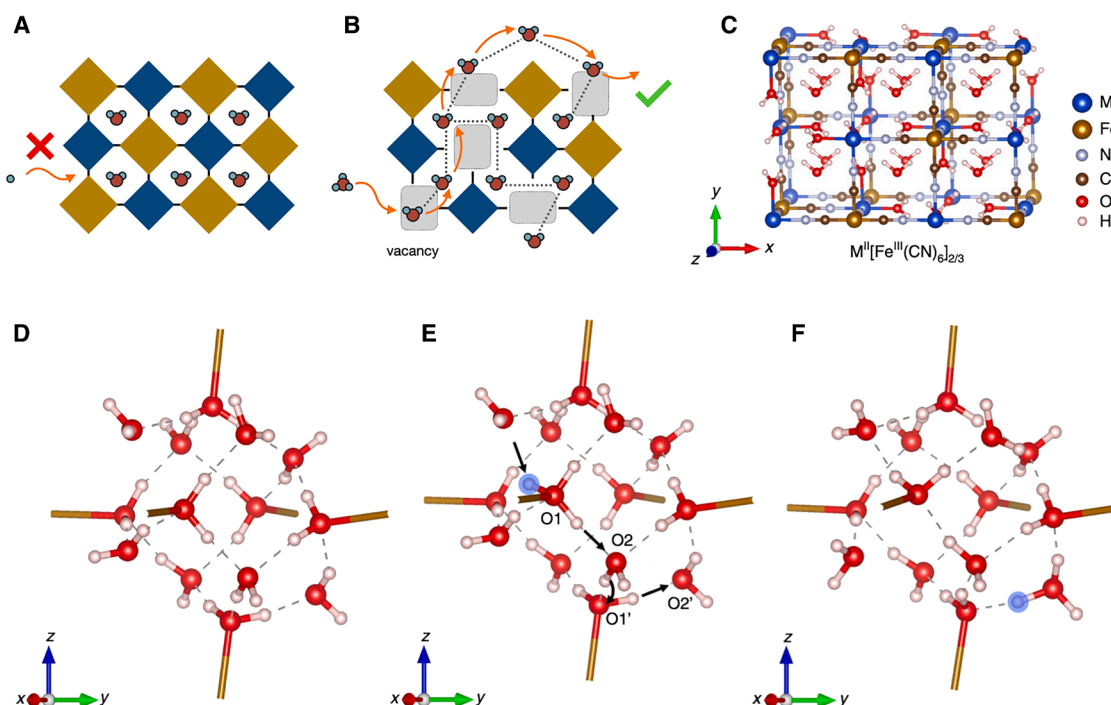


Figure 7. Proton transfer in PBAs

(A and B) Schematic diagram of PBA optimization for proton transfer, the integrated structure blocks water molecules, and the deficiencies introduce more water molecules for continuous H-bond network.

(C) Structure of CuFe-TBA with vacancies, which presents 3D topological network for H-bonds.¹¹

(D–F) Proton bonding and transfer steps in CuFe-TBA. O1 represent ligand water, and O2 represents zeolitic water.¹¹

mAh g^{-1} in 6 M H_2SO_4 electrolyte.⁵¹ This enhanced capacity is attributed to the presence of a double-redox center ($\text{V}^{\text{III}} \leftrightarrow \text{V}^{\text{IV}} \leftrightarrow \text{V}^{\text{V}}$, $\text{Fe}^{\text{II}} \leftrightarrow \text{Fe}^{\text{III}}$) within the VHCF structure. Furthermore, the open framework of the V-containing PBA promotes the formation of an extensive internal H-bond-network topology. This network creates potential solid-state pathways for proton conduction via the Grotthuss mechanism, facilitating both pseudo-capacitive charge storage and rapid proton-diffusion kinetics. The VHCF material exhibits good rate capability, retaining 60% and 43% of its capacity at 100 C and 200 C rates, respectively. These findings inspire further research into the design and exploration of novel materials with optimized structures for efficient proton-storage mechanisms.

WO_3

Layered and two-dimensional (2D) materials hold significant promise in electrochemistry due to their high specific surface area and abundance of redox-active sites. Researchers have placed particular interest in understanding the critical relationship between surface atoms and interlayer water molecules (Figures 8A and 8B). The tungsten oxide family serves as a good example owing to its structural versatility with diverse polymorphic configurations and the capability for modulation of interlayer water content.

Researchers have explored the incorporation of water molecules into the pores of conductive hydrous hexagonal tungsten oxide (h-WO_3), a layered nanostructure, to achieve large-scale proton transmission.⁵² The inspiration has been drawn from

the remarkable proton transport facilitated by single-file water chains within protein molecules, which act as a "highway" for proton movement (Figure 8C). Studies have revealed that water-containing samples exhibit enhanced capacity, which is derived from both water molecules and the resulting H-bond chains. Experimental data suggested that a minimum of 0.5 water molecules per WO_3 unit is necessary for the formation of single-file water chains, which are essential for supporting Grotthuss-type proton motion. $\text{h-WO}_3 \cdot n\text{H}_2\text{O}$ demonstrates an impressive proton conductivity of $\sim 1.0 \text{ mS cm}^{-1}$ at 22°C , rising to 2.7 mS cm^{-1} at 60°C and 3.7 mS cm^{-1} at 90°C .⁵⁵ The calculated activation energy of $0.12 \pm 0.02 \text{ eV}$ closely resembles the value observed in bulk water (0.11 eV), further supporting the notion of a similar transport mechanism, namely the Grotthuss mechanism.

Besides, the layered material in the WO_3 family presents a fascinating example for studying the interplay between hydration, proton transport, and aqueous H-bonding networks. It has been reported that the anhydrous $\gamma\text{-WO}_3$ shows inferior performance for proton storage than the two hydrous phases, i.e., $\text{WO}_3 \cdot 1\text{H}_2\text{O}$ and $\text{WO}_3 \cdot 2\text{H}_2\text{O}$.⁵³ Interestingly, the lattice water in hydrous phases is highly confined with only limited local conformational freedom rather than translational one. These consecutive water networks play a role in changing the pathway of structural transformation. It isolates the electrochemically driven structural transformations to two dimensions within the $\text{WO}_5(\text{OH}_2)$ octahedral network, leading to very little change in

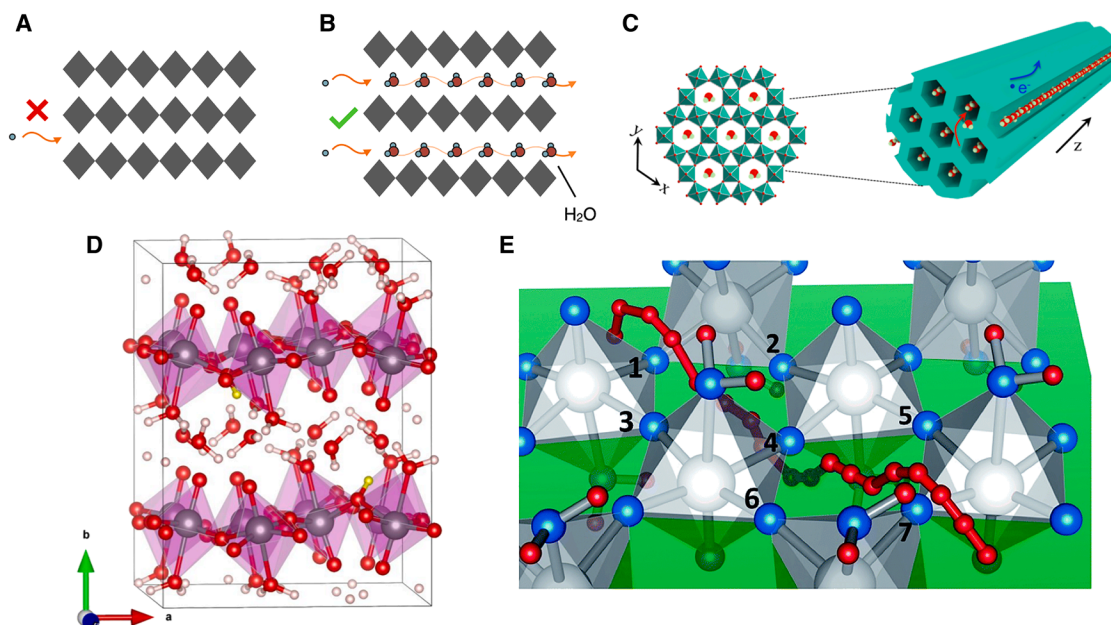


Figure 8. Proton transfer in layered materials

(A and B) The optimization of H-bond network for proton-transfer pathway in layered WO_3 .

(C) Structure of h-WO_3 with tunnel water molecules; sufficient water (0.5 water per WO_3 unit) can form continuous single-file water chains.⁵²

(D) Structure of layered $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ with proton bonding to crystal oxygen.⁵³

(E) Proton-transfer steps through crystal oxygen in $\text{WO}_3 \cdot 2\text{H}_2\text{O}$.⁵⁴

interlayer spacing with proton intercalation. In contrast, without water networks, the structural transformation of $\gamma\text{-WO}_3$ to the tetragonal structure of H_xWO_3 is sluggish and incomplete, which becomes the rate-limiting process of proton transfer. However, it is believed that the proton transport is mainly related to the terminal O ions in the $[\text{WO}_6]$ tetrahedron rather than the O in water molecules (Figures 8D and 8E).⁵⁴ This case provides another possibility for the effect of water networks, in which water molecules indirectly influence the proton motion. Nevertheless, the proton-transfer model remains controversial and requires further study. The family of WO_3 exhibits high redox activity and a highly reversible capacity for proton intercalation/deintercalation, which may help to discover new electrode materials.

MXenes

MXenes are a class of 2D TM carbides, nitrides, or carbonitrides (M represents TMs like Ti and V; X represents C and N), and they have garnered significant interest due to their unique 2D structure and rich functionality. The pre-intercalated water enables fast proton-transport capability (Figure 9A).⁵⁶ Researchers have employed *ab initio* molecular dynamics (AIMD) simulations to shed light on the mechanism of proton behavior between MXene layers and the influence of the surrounding aqueous environment.⁵⁷ The computational results reveal that reversible proton redox reactions occur between surface O sites on the MXene and interfacial water molecules. The transfer of protons follows the Eigen-Zundel-Eigen mechanism, consistent with the Grotthuss model in bulk water.

Experimental studies have been conducted to further validate the role of water molecules in proton transport.⁵⁸ These

studies confirmed that water molecules confined between MXene layers are responsible for establishing H-bond networks that facilitate rapid proton diffusion. It was suggested that water molecules and hydronium ions organize into a well-defined configuration characterized by a uniform network of H-bonds (Figures 9B and 9C). Additionally, the dipole orientation of these molecules and ions exhibits a high degree of alignment around 90° , indicative of a planar arrangement that optimizes proton motion. In contrast, the surface functional groups on MXenes, primarily hydroxyls in this case, disrupt the H-bond networks. This disruption leads to a heterogeneous distribution of water molecules and a more discrete network of H-bonds. Since the Grotthuss mechanism relies on the continual breaking and reformation of H-bonds for proton transport, an excessive number of hydroxy groups can impede this process by strongly fixing the H-bonds in place.

Further studies have explored the migration behavior of protons between $\text{Ti}_3\text{C}_2\text{T}_x$ layers in the presence and absence of water.⁵⁹ These investigations revealed that water has a significantly greater influence on proton diffusion than other cations. Water effectively reduces the migration energy barrier for protons and expands the available pathways within the 3D space. Collectively, these findings strongly support the conclusion that water-mediated Grotthuss proton hopping is the dominant mechanism for proton transport in MXenes. The research has also highlighted promising directions for future studies, focusing on how to leverage this mechanism to optimize the proton insertion/extraction capacity of MXene electrodes for electrochemical applications.

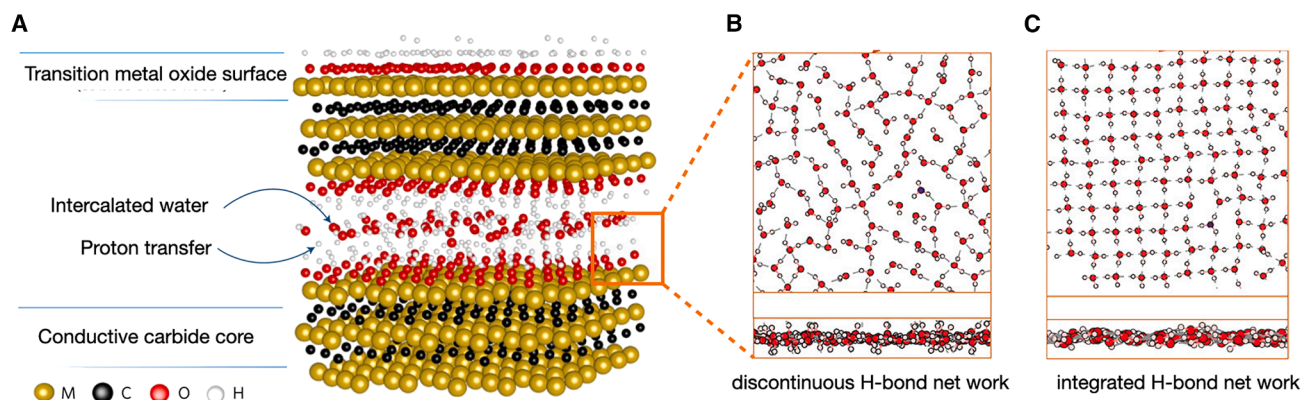


Figure 9. Proton transfer in MXenes

(A) Structure of MXenes with interlayer water, which interact with terminal groups.⁵⁶

(B) Disturbance of water-based H-bond network in pristine MXene.⁵⁸

(C) Integrated H-bond network in modified MXene.⁵⁸

Proton-transfer reinforcement via non-water H-bonds

The Grotthuss mechanism for proton transport offers a versatile strategy for achieving rapid proton movement in various systems. Crucially, this mechanism is not restricted to water-based H-bond networks. The exploration of non-aqueous H-bond networks presents an exciting avenue for the development of fast proton-storage materials for aqueous batteries. By incorporating alternative H-bond donors and acceptors into battery materials, researchers can potentially engineer robust proton-transport pathways that rival those observed in water. Such a mechanism was first discovered in MoO_3 , a typical anode material for full-proton batteries. Then it was grafted in manganese oxides and vanadium oxides, thus expanding the application scope of proton storage.

MoO_3

$\alpha\text{-MoO}_3$ is a layered TM oxide that has emerged as a promising electrode material for proton batteries due to its exceptional rate performance.⁶⁰ This material exhibits a specific capacity of 125 mAh g^{-1} at 5 C and a remarkable 88 mAh g^{-1} even at an ultrahigh rate of 100 C (tested in 4.4 M H_2SO_4 electrolyte³⁵). These impressive results highlight $\alpha\text{-MoO}_3$ as a promising candidate for next-generation proton batteries. Experimental evidence suggests that the charge storage mechanism in $\alpha\text{-MoO}_3$ is primarily diffusion controlled.³⁵ The process involves the intercalation and deintercalation of protons, leading to the formation of hydrogen molybdenum bronzes (HMBs, H_xMoO_3 , where $0 < x < 2$). Although there remains controversy about the precise value of proton intercalation, the consensus for phase transition of MoO_3 has been achieved (Figure 10A). It is accepted that pristine MoO_3 undergoes a conversion reaction within the first protonation, while the orthorhombic structure is transformed into the monoclinic phase. After that, subsequent charging and discharging cycles reveal a limited ability to fully extract protons back to the original $\alpha\text{-MoO}_3$ phase.⁶¹ Some papers suggested that the full protonation value is $x = 0.88$,⁶¹ while other values, such as $x = 1.68$,³⁵ 1.75,⁶² and 2.5,⁶³ have also been reported.

Since the proton-transfer pathway is of vital importance for the electrochemical performance, researchers have carefully inves-

tigated the diffusion pathways of protons. There are three favorable adsorption sites in MoO_3 and protonated MoO_3 (Figures 10B and 10C), which can be denoted as A ($\text{O2-H}\cdots\text{O2}$), B ($\text{O1-H}\cdots\text{O1/O2}$), and C (O2-H-O1).⁶³ Here, O1 represents the terminating O ion that coordinates to 1 Mo, and O2 represents the bridging O that coordinates to 2 Mo. The increased bonding sites complicate proton behavior because the intercalation and deintercalation of protons would distort the lattice. In turn, the distorted lattice, especially with the change in O–O distances, influences the proton-transfer efficiency. Specifically, the intercalation of protons follows the sequence of A (0.5 H^+), B (1.5 H^+), and C (0.5 H^+). In contrast, the deintercalation of protons follows a different sequence of C (0.25 H^+), A (0.5 H^+), B (0.75 H^+), and B + C (1.0 H^+). These asymmetric pathways explain the asymmetric charge/discharge profile. As shown in Figure 10B, the protonation of MoO_3 and deintercalation of $\text{H}_{2.5}\text{MoO}_3$ initiate from very different states. Protons tend to transfer between the adjacent O atoms that present the lowest distances. Fortunately, in MoO_3 these O–O distances are shorter than 2.9 Å, which accounts for the fast Grotthuss-type diffusion of proton.

A recent study sheds light on this critical aspect by revealing the formation of non-water H-bond networks that facilitate proton motion via the Grotthuss mechanism.⁶² In this work, the authors electrochemically activated $\alpha\text{-MoO}_3$ to a deeper depth of discharge, leading to the formation of a new orthorhombic $\text{H}_{1.75}\text{MoO}_3$ phase (Figure 10D). This phase exhibits significant lattice distortion, evident from the increased d -spacings along the [010] and [001] directions, as well as the expansion of the (101) planes. As a consequence, when a proton is intercalated and bonded to a terminal O atom, it can form new H-bonds with neighboring terminal O atoms within a close proximity of only 0.24 nm. In essence, the structural distortion creates interconnected H-bond networks mediated by these terminal O atoms (Figure 10E). Theoretical calculations revealed that, due to the distorted structure, a single proton can be simultaneously connected to two neighboring terminal O atoms during this transition state, resembling the behavior observed in the Grotthuss mechanism involving water molecules. The calculated low activation energy of 0.14 eV further supports

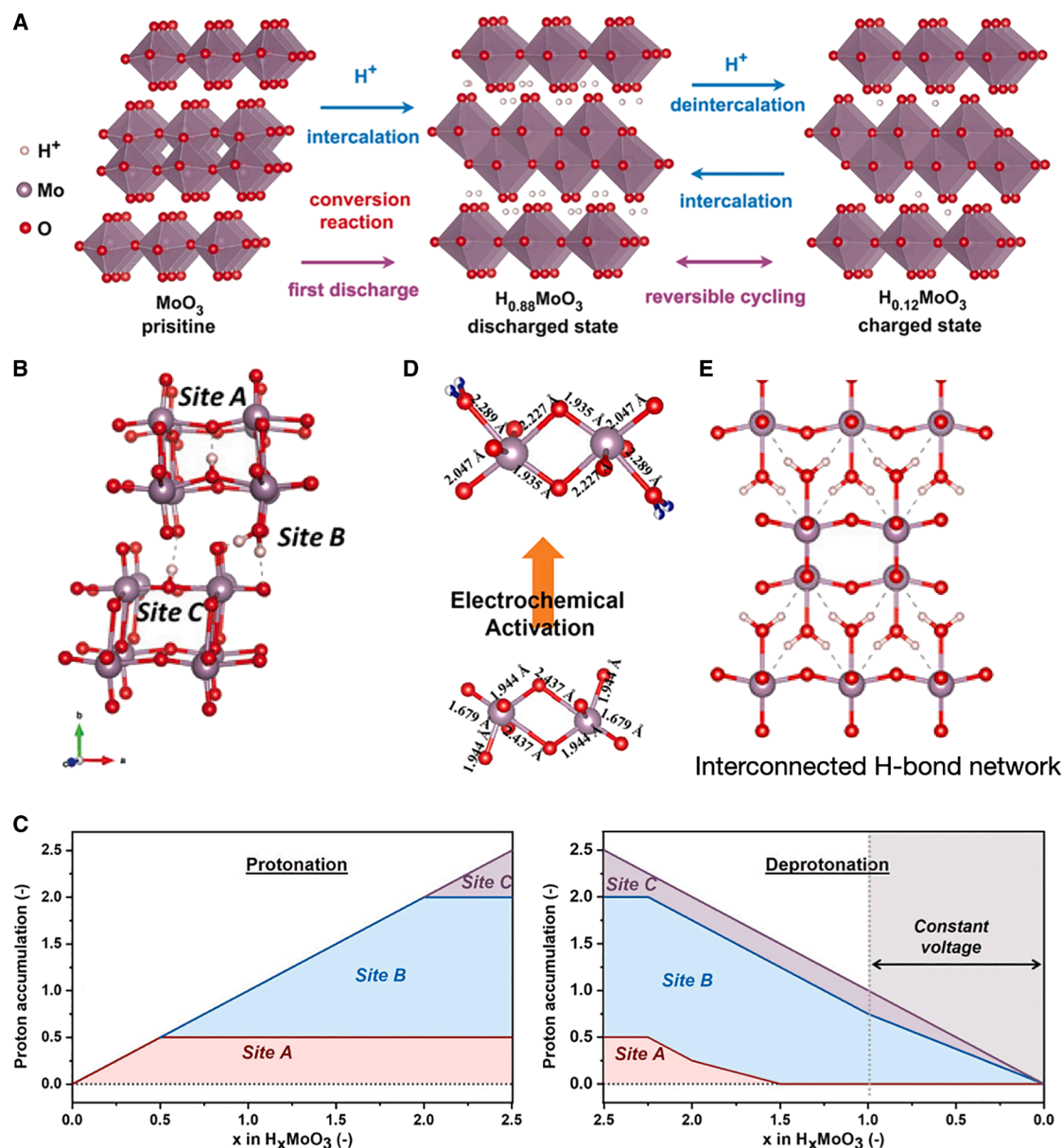


Figure 10. Proton transfer in MoO_3

(A) Phase transition of α - MoO_3 during electrochemical cycles.³⁵

(B) Proton sites and pathways in H_xMoO_3 .⁶³

(C) Proton transfer follows different sequences in intercalation and deintercalation processes.⁶³

(D) Topological structure transformation of α - MoO_3 after electrochemical activation.⁶²

(E) Interconnected H-bond network between terminal oxygens in α - MoO_3 .⁶²

the notion of fast kinetics. Consequently, the electrode exhibits reversible cycling between the $\text{H}_{1.75}\text{MoO}_3$ and $\text{H}_{0.19}\text{MoO}_3$ phases. Additional calculations predict near energy-free diffusion, where protons within $\text{H}_{1.75}\text{MoO}_3$ spontaneously migrate to proton-deficient regions after a certain relaxation time. This Grotthuss-type proton motion not only enhances diffusion kinetics but also contributes to the structural stability of the material. The optimized α - MoO_3 electrode delivers an outstanding capacity of 111 mAh

g^{-1} at a remarkable rate of 2,500 C for 5,000 cycles, ranking among the highest capacities reported for proton battery materials.

V_2O_5

Similar to α - MoO_3 , non-water H-bond networks offer a promising approach to promote proton diffusion and storage in aqueous ZIBs. A few years ago, researchers explored pre-intercalating ammonium ions (NH_4^+) into V_2O_5 to expand the interlayer spacing

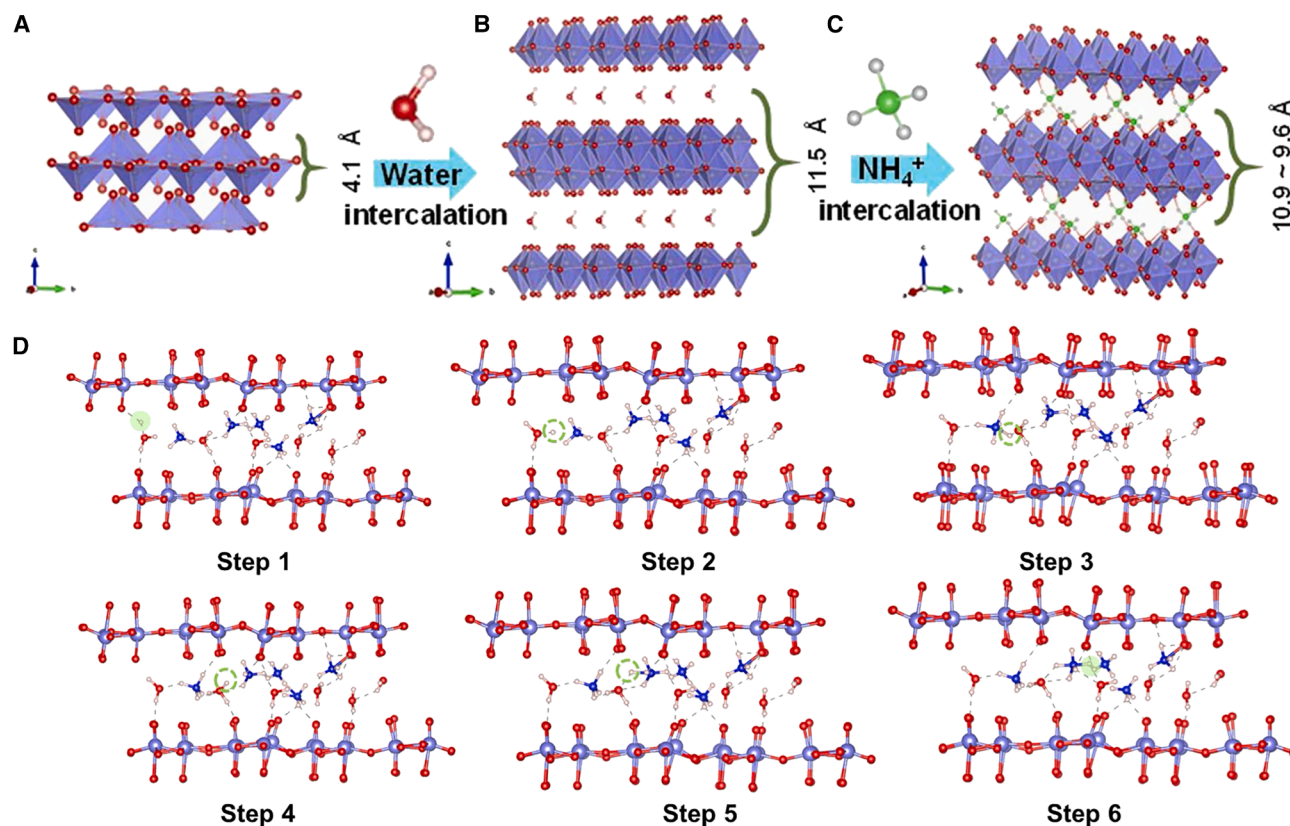


Figure 11. Proton transfer in V_2O_5

(A–C) Crystal structure of pristine V_2O_5 , H_2O -intercalated V_2O_5 , and NH_4^+ -intercalated V_2O_5 .⁶⁵
(D) Proton-transfer pathway through NH_4^+ -based H-bond network.⁶⁵

and facilitate zinc-ion uptake/removal.⁶⁴ While this study identified the presence of OH^- -related byproducts, the potential contribution of proton intercalation was not fully explored.

Recently, this concept has been revisited and a refined synthesis method was employed to precisely control the amount of pre-intercalated NH_4^+ ions through precursor selection.⁶⁵ Computational analysis revealed that the bond lengths within the ammonium-related H-bond networks range from 1.6 to 1.8 Å (Figures 11A and 11C), which are shorter than those observed in water-based networks (1.9–2.0 Å, Figure 11B). This finding suggests that the H-bond networks are partially formed by NH_4^+ ions, leading to enhanced stability compared to pristine networks solely composed of water molecules as reported in earlier studies. Furthermore, the strong interlayer bonding energy helps to mitigate V-element dissolution and structural collapse during cycling. These ammonium-based H-bond networks serve as efficient diffusion pathways for protons, where proton transport occurs via the breaking and reformation of H-bonds following the Grotthuss mechanism (Figure 11D). In contrast, bare V_2O_5 relies on direct hopping of protons between adjacent O atoms, a process associated with significantly higher diffusion-energy barriers. This study also highlights the importance of optimizing the concentration of NH_4^+ ions within the crystal structure. Insufficient NH_4^+ ions

cannot establish effective transport networks, while an excessive amount can solidify the H-bond network, hindering proton diffusion. These theoretical predictions align well with the experimental observations. The optimized material delivers an impressive capacity of 563 mAh g^{-1} with an intercalation of 1.44 protons per unit formula and exhibits a remarkable cycling performance, retaining 85% of its capacity after 4,000 cycles in 3 M $\text{Zn}(\text{OTf})_2$ electrolyte. This work provides valuable insights into the role of ammonium-based H-bond networks in energy-storage materials. Furthermore, it establishes a versatile strategy for promoting proton storage in aqueous batteries, potentially applicable to a broader range of electrode materials.

MnO_2

The discovery of proton contributions to the electrochemical behavior of MnO_2 polymorphs has sparked significant research interest in understanding the mechanisms of proton storage and transport within these materials. The work mentioned above verified the proton-storage sites within $\alpha\text{-MnO}_2$,⁴⁰ but it did not provide the transfer pathways, let alone the improvement strategies. Some literature reported that dehydrated MnO_2 samples exhibit less proton insertion even in mild-acid environments.⁶⁶

Our group has explored the strategic application of non-water H-bond networks to promote proton transport within $\alpha\text{-MnO}_2$ cathodes.⁴⁶ We successfully synthesized Ni-doped tunnel-type

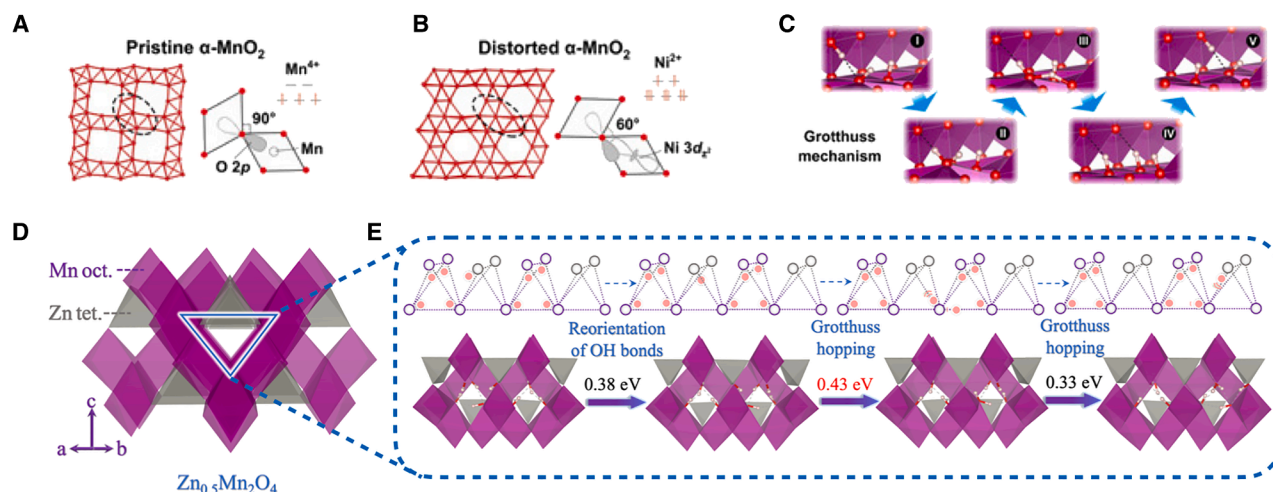


Figure 12. Proton transfer in water-free MnO₂

(A) Crystal structure of α-MnO₂ and electronic configuration of Mn⁴⁺ ion.⁴⁶
 (B) Crystal structure of Ni-doped α-MnO₂ and electronic configuration of Ni²⁺ ion. The Ni doping enhances the distortion of [2 × 2] tunnels.⁴⁶
 (C) Proton-transfer steps through crystal distortion-induced H-bond network.⁴⁶
 (D) Crystal structure of Zn_{0.5}Mn₂O₄ spinel.¹²
 (E) Proton-transfer steps through Zn-vacancy-induced H-bond network.

α-MnO₂ using a simple one-step hydrothermal reaction. This approach leverages the distinct electronic configurations of Mn⁴⁺ (t³_{2g}e⁰_g) and Ni²⁺ (t⁶_{2g}e²_g) ions within an octahedral coordination environment (Figures 12A and 12B). According to crystal-field theory, the high-energy e_g orbitals (d_{x²-y²} and d_{z²}) are antibonding. Doping the α-MnO₂ lattice with 5% Ni²⁺ ions introduces two additional electrons into the e_g orbitals, strengthening the metal-oxygen interactions. This phenomenon weakens the stability of the tetragonal lattice and induces structural distortion. Furthermore, the occupied d_{z²} orbital of the Ni²⁺ ion exhibits weaker spatial overlap with the O 2p orbital compared to Mn⁴⁺. This weaker overlap leads to a polarization of the O 2p electrons toward the octahedral sites. TEM confirms significant tetragonal oxide (TO) distortion in the Ni-doped MnO₂ samples. This distortion brings the O atoms located within the walls of the [2 × 2] tunnels closer together, creating favorable sites for consecutive proton diffusion via H-bond formation. Computational calculations reveal a detailed five-step diffusion pathway for protons within the Ni-doped α-MnO₂ structure (Figure 12C). This process exhibits an exceptionally low energy barrier of only 0.55 eV, a stark contrast to the significantly higher values observed for pristine MnO₂ (1.28 eV in [2 × 2] tunnels and 0.83 eV in [1 × 1] tunnels). This low energy barrier signifies a Grotthuss-type proton-transport mechanism, facilitating rapid proton uptake and removal within the cathode. Consequently, the energy density of the Ni-doped α-MnO₂ electrode is improved by 25%.

Inspired by the success of lattice tuning, we grafted this strategy to ZnMn₂O₄ spinel.¹² It is a common phase transition product of MnO₂, traditionally undervalued in aqueous-battery applications due to its lack of crystal water and low proton-transfer capabilities. Our research group has recently addressed this challenge by developing a novel proton-conductive Zn-Mn-O spinel with enhanced performance. This material, Zn_{0.5}Mn₂O₄,

incorporates Zn vacancies at half of the available Zn sites within the spinel structure (Figure 12D). The presence of these vacancies triggers a unique proton-transport mechanism. When four protons become bonded to the O atoms and occupy the Zn-vacant 8a site, electrostatic repulsion within this proton-rich tetrahedron induces the neighboring O atom to bond with additional protons in the form of –OH₂ groups. This configuration then undergoes a de-excitation process, transforming into a stable –OH moiety and releasing one proton to a nearby site. Remarkably, this proton-hopping process requires only 0.47 eV, representing less than half of the energy consumption compared to conventional consecutive hopping mechanisms. This facile proton transport occurs not only at the boundary between proton-rich and proton-poor regions but also within the interior of the proton-rich domains. Consequently, protons cooperate in a Grotthuss-type manner, hopping through the 3D tunnel network of the spinel structure (Figure 12E). This efficient proton-delivery mechanism allows the material to deliver a high capacity of 299.7 mAh g^{−1} while maintaining excellent structural stability (in 3 M ZnSO₄+0.2 M MnSO₄ electrolyte). It has been pointed out that the sluggish proton diffusion in electrodes is always the limiting step for proton storage, rather than the lack of storage sites. By strategically introducing structural variations, such as vacancies, it is possible to promote Grotthuss proton transport without relying on crystal water.

To sum up, proton transfer in solid electrode materials can be enhanced by activating Grotthuss-type transfer mode, which is realized by introducing proper H-bond network. According to the storage sites mentioned in the last section, the H-bond network can be composed of consecutive water molecules or new structural distortions in which no water participates. This strategy can be applied in not only full-proton battery materials, such as WO₃ and MoO₃, but also in aqueous metal-ion battery

materials, such as MnO_2 , PBAs, and V_2O_5 . The modified electrodes that make better use of proton transfer always present higher performance in capacity, rate, and durability. This approach holds significant promise for the development of next-generation high-performance aqueous-battery materials.

PROTON TRANSFER IN AQUEOUS ELECTROLYTES

Proton-transfer enhancement for conductivity improvement

High electrolyte conductivity is paramount for all battery systems, as it enhances both electrochemical kinetics and Coulombic efficiency (CE). Conductivity is governed by the interplay between the driving forces (electric field and concentration gradient) acting on ions and the opposing frictional forces. For most metal ions, their bulky hydration shells create significant steric hindrance, limiting their mobility in electrolytes. Protons, however, circumvent this limitation due to their unique ability to participate in the Grotthuss mechanism, enabling rapid movement without significant changes in the surrounding solvation structure. This exceptional proton mobility translates to high conductivity, a key advantage for proton batteries.

There seem to be very few ways to enhance proton transfer, except for manipulating the concentration of electrolytes, since the precondition of proton transfer is the combination of sufficient protons and water molecules. Most of the full-proton batteries employ highly soluble inorganic acids as electrolytes due to their ability to facilitate fast proton motion through extensive H-bond networks. For dilute acid solutions, experiments have confirmed an inverted V-shaped relationship between room temperature conductivity and concentration (Figure 13A).⁶⁷ A maximum conductivity is usually observed at a concentration around 10 mol %. This implies that conductivity depends not only on the carrier density but also on the solution structure (Figure 13B). Before the peak, the solution structure is water dominated, and protons are primarily transported along the H-bond network of water. After the peak, the structure transitions to a non-aqueous structure, including anhydrous liquid acid or the melt of crystals, and the proton-transport mechanism becomes more complex. It should be noted that, even in dilute solutions, the water-based proton transfer has not been clearly revealed. Experimental evidence suggested the presence of structurally diverse, dynamically distorted complexes resembling Eigen and Zundel cations, but there is a controversy surrounding the dominance of Eigen or Zundel cations.^{68–70} In most cases, the solvation structure of hydrated excess protons is more intricate than simply Eigen or Zundel cations. These structures represent limiting cases within a spectrum of configurations, with numerous intermediate states existing due to the dynamic nature of the solvation shell (Figures 4D and 4E).

For highly concentrated acid solutions or non-aqueous acids, the solvation structure deviates significantly from that observed in dilute aqueous solutions.⁷¹ For example, phosphoric acid can form very strong H-bonds, leading to a highly ordered structure with sluggish proton dynamics and consequently, lower proton conductivity. Paradoxically, neat liquid phosphoric acid possesses the highest intrinsic proton conductivity of any known material. This seemingly contradictory behavior can be attrib-

uted to the complex interplay between phosphoric acid molecules (H_3PO_4), as well as their variations such as H_2PO_4^- and H_4PO_4^+ , and solvent molecules. Overall, the proton-transfer behavior does not always follow a strict pattern. Instead, once a proton is accepted by a Grotthuss chain, the polarization of the chain is disturbed. Then H-bond network suffers complex local breakage and reconstruction.^{72,73} The interplay between these chains and a network of frustrated H-bonds ultimately gives rise to the exceptional proton conductivity observed in neat phosphoric acid. In contrast, sulfuric acid (H_2SO_4) possesses a limited number of hydrogen atoms, hindering the formation of a robust H-bond network for efficient diffusion of protons.

While high proton conductivity is undeniably beneficial for battery performance, it is crucial to strike a balance between efficient proton transport and electrolyte stability. Unrestrained attempts to simply maximize proton transfer can have detrimental consequences. Increased proton mobility can inadvertently lead to enhanced proton-related side reactions, ultimately compromising the stability of the electrolyte. These detrimental side reactions will be explored in the following section.

Proton-transfer resistance for expansion of electrochemical stability window

One significant limitation of aqueous batteries is their low operating voltage, directly tied to the narrow electrochemical stability window (ESW) of water. Thermodynamically, water itself remains stable only within a potential window of approximately 1.23 V. Beyond this limit, water electrolysis occurs, leading to the production of oxygen (OER) at high potentials and hydrogen (HER) at low potentials.⁷⁴ This narrow ESW not only limits the choice of suitable electrode materials and the types of electrochemical redox reactions but also leads to the formation of gaseous products and a degradation of the electrolyte.⁷⁵

For proton-based batteries, the electrolytes are always acidic, which is more vulnerable to HER.⁷⁶ One promising approach to address this limitation involves the introduction of additives that can establish new H-bond networks.^{77–80} Organic molecules containing functional groups that act as either H-donors (e.g., hydroxy groups) or acceptors (e.g., electronegative groups) can be strategically incorporated to reinforce the existing H-bond network within the electrolyte. This strategy effectively broadens the ESW by enhancing its stability. Our previous research has explored the use of ethylene glycol (EG) as an effective additive for HER suppression in aqueous ZIBs.⁸¹ Compared to water molecules, each EG molecule possesses two hydroxy groups, which can participate in additional H-bond interactions. This effectively strengthens the H-bond network within the ZnSO_4 electrolyte. The additional hydroxy groups can function as both proton donors and acceptors, hindering proton mobility.⁸² Consequently, the introduction of EG suppresses HER at the anode and improves the CE. In a following study, we investigated the electrochemically polymerized polyacrylamide (PAM) hydrogel as an electrolyte skeleton (Figure 13F).⁸³ The PAM hydrogel scaffold features abundant acyl groups ($-\text{C}=\text{O}$) that can act as both H-bond donors and acceptors ($-\text{NH}_2$). Raman spectroscopy confirmed a significant enhancement of the H-bond network within the electrolyte

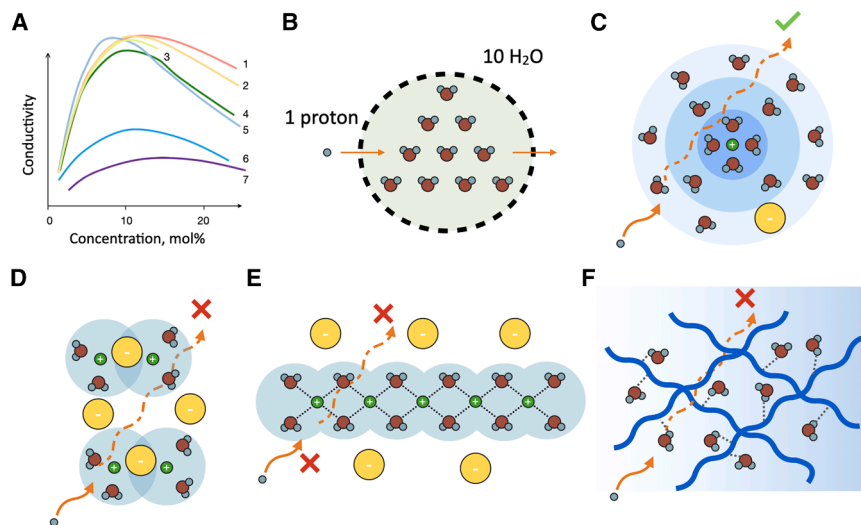


Figure 13. Proton transfer in electrolytes

(A) Relationship between room-temperature conductivity and concentration (1, HNO₃; 2, HCl; 3, HBr; 4, HClO₄; 5, H₂SO₄; 6, HIO₃; 7, H₃PO₄).⁶⁷

(B) Schematic diagram of ratio of proton and water molecules, at the acid concentration that presents highest conductivity.

(C) Schematic diagram of proton-transfer pathway in dilute electrolyte.

(D) Schematic diagram of proton-transfer pathway in LiTFSI water-in-salt electrolyte.

(E) Schematic diagram of proton-transfer pathway in LiNO₃ water-in-salt electrolyte.

(F) Schematic diagram of proton-transfer pathway in hydrogel electrolyte.

upon the introduction of PAM. It should be noted that, within the new H-bond network, the H atom in organic additives cannot easily disconnect from basement, thus working as fixed obstruction in proton-transfer pathway. The net effect of PAM is therefore the suppression of proton transfer.

High-concentration electrolytes (HCEs) represent another promising strategy for restricting proton motion but with different mechanism.⁸⁴ The first aqueous HCE was reported to utilize lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) at a concentration of 21 mol kg⁻¹. This system contains only a limited amount of free water (approximately 16%), leading to a significant reduction in the number of available H-bonds (Figures 13C and 13D). HCEs also modify the hydration shell of Li ions. Within an HCE, TFSI⁻ anions can directly coordinate with Li ions in the primary solvation shell. This disrupts the typical water-water H-bond network surrounding Li ions, leading to a new arrangement where Li ions are connected by a combination of shared TFSI⁻ anions and water molecules. As a consequence of these changes, the ESW is significantly expanded to 3.0 V. This wider window enables the utilization of low-potential anode materials such as Mo₆S₈, ultimately leading to a substantial increase in the power density of the entire battery. Following this initial work, extensive research has been conducted on various HCE systems,^{85–88} all aiming to achieve a similar outcome: lowering the water content and hindering the formation of water-based H-bonds within the electrolyte. Such strategy employs much more cations and anions to break the continuity of the H-bond network, thus impeding proton's Grotthuss-type transfer.

Our research group has proposed a novel perspective, suggesting that kinetic factors can, in some cases, play a dominant role in determining the ESW of aqueous electrolytes. We have investigated lithium nitrate (LiNO₃) solutions at various concentrations using a combination of theoretical calculations and spectroscopic analyses.⁸⁹ In dilute LiNO₃ solutions, Li ions primarily coordinate with four water molecules, forming Li(H₂O)₄ complexes. As illustrated in Figure 13E, only a small percentage (1.9%) of water molecules are shared by pairs of Li ions. A larger

fraction (16.1%) interacts with isolated Li ions, while the remaining water molecules form a vast H-bond network. However, as the salt concentration increases, a growing number of Li ions appear in pairs, sharing their primary solvation shells. At a concentration ratio of LiNO₃ to water of 1:2, the free water molecule content plummets to a mere 1.2%. Under these conditions, most water molecules become incorporated into extended linear chains of Li ions, leading to the near-complete disappearance of H-bonds. It is revealed that, at super-concentrations, a unique local structure characterized by intimate Li-water interactions emerges. This structure involves the formation of polymer-like (Li(H₂O)₂)_n chains, which replace the ubiquitous H-bond network between water molecules, exhibiting similarities to the crystal structure of solid LiNO₃·3H₂O. Certainly, it eliminates the precondition of fast transport of protons. ESW is expanded to 2.55 V in this low-cost, super-concentrated LiNO₃ electrolyte. This discovery holds significant promise for advancing the fundamental understanding and development of HCEs.

It should be noted that the relationship between high salt concentration and H-bond elimination in aqueous electrolytes appears counterintuitive. Recent research investigating the water dynamics and structure of LiCl solutions sheds light on this phenomenon.⁹⁰ While it is true that highly concentrated LiCl solutions disrupt the bulk water H-bond network, the study reveals that the limited H-bonds remaining in these concentrated systems are, on average, stronger than those found in bulk water. This seemingly contradictory behavior can be attributed to the formation of solvent-separated ion pairs. In these pairs, two water molecules bridge oppositely charged ions. The electrostatic interactions between the lone pairs of electrons on the water molecules and the ions lead to increased partial charges on the water molecules. These enhanced partial charges, in turn, strengthen the H-bonds between the water molecules. The analysis of frequency-dependent anisotropy decays supports this explanation. Water molecules engaged in stronger H-bonds exhibited significantly slower diffusion and greater angular restriction. Furthermore, the magnitude and frequency dependence of these restrictions decreased as the LiCl concentration (molar ratio) was reduced, further corroborating the link between stronger H-bonds and concentrated solutions. In a word, the

manipulation of proton transfer via H-bonds in electrolyte requires further study. As mentioned above, arbitrary reduction of proton activity also impacts the electrolyte conductivity of the battery. It seems a stubborn headache for energy-density improvement in aqueous systems, and the proton activity should be carefully modulated for appropriate balance of both conductivity and ESW.

PROTON TRANSFER AT THE ELECTRODE/ELECTROLYTE INTERFACE

Surface reconstruction and proton transfer at electrode side

The interface between the electrode and electrolyte in batteries plays a critical role in governing electrochemical reactions.⁹¹ It serves as the stage for a multitude of complex processes, including charge transfer, material conversion (synthesis/decomposition), and mass transport.⁹² In aqueous environments, the high reactivity and facile conversion of water/proton/hydronium ions pose a significant challenge to the stability of solid electrode materials. However, the lack of direct, *in situ* characterization techniques hinders a precise understanding of the interfacial dynamics.

A detailed study of the interface reconstruction in the MoO₃ system uncovered the crucial role of water adsorption at the electrode interface.³⁵ Upon immersion in an aqueous environment, MoO₃ electrodes typically undergo specific water adsorption. Studies using electrochemical quartz crystal microbalance (EQCM) have revealed the presence of additional water species adsorbed onto the MoO₃ surface after a short immersion period, even without any applied electrochemical reactions (Figure 14A). As a polar solvent, water molecules may be coordinated with metal ions at the places where crystallographic symmetry is broken. Then these water layers establish a new H-bond network at the electrode surface. ¹H solid-state nuclear magnetic resonance verifies that the new H-bond presents medium strength, which is differentiable with the stronger one in bulk electrode and the weaker one in bulk electrolyte. Such surface reconstruction bridges the electrolyte and the electrode, facilitating proton transfer at the interface. Further investigation through electrochemical cycling observes the continuous generation of H-bonded species at the MoO₃ interface. Some other electrode materials, such as WO₃, also undergo water adsorption at the electrode surface.⁵⁵ Besides, in mild electrolytes, some byproducts also emerge at the electrode surface, but their influence on proton motion requires further study.⁴⁶

Interestingly, experimental evidence proved that proton transfer does influence the water adsorption behavior. The de-protonation processes lead to enhanced water adsorption at the electrode surface, which is deduced by the mass increase of the electrode. This phenomenon can be attributed to a "vehicle-type" proton-motion mechanism. As hydrated protons are transferred from the electrode toward the bulk electrolyte, other water molecules move in the opposite direction and become adsorbed at the interface. Since most literature about vehicle mechanisms do not focus on proton batteries, this study provides valuable insights into the role of vehicle-type proton motion in interfacial reconstruction and

sheds light on the complex interplay between water and proton transport within the aqueous-battery interface.

Recent research has explored strategies to reinforce H-bond networks at the interface, inspired by the critical role of proton transport in these systems.⁹⁵ The study employed oxygen plasma treatment to introduce functional groups, such as hydroxyl (OH) and carboxyl (COOH), onto the MoO₃ surface (Figure 14B). This modification was confirmed by Fourier transform infrared (FTIR) spectroscopy, which reveals an enhanced signal corresponding to O–H bonds. Furthermore, the vibrational modes of water molecules adsorbed at the interface shift from symmetric to asymmetric, indicating the formation of a more complex H-bond network. These O-containing functional groups act as bridges between the electrode and electrolyte, facilitating smoother proton transfer across the interface. Consequently, the pre-treated MoO₃ electrodes exhibit lower charge-transfer resistance and a significantly improved capacity for proton storage, even when utilizing low-concentration proton electrolytes.

In summary, the electrode-material interface undergoes reconstruction in aqueous solutions, leading to changes in the H-bond network at the interface, which may be beneficial for proton transport. Additionally, artificially enhancing the H-bond network at the interface can promote proton transport. Although this interface-optimization strategy is not yet widely used, we believe it is crucial for achieving high-performance proton batteries, and it will also play a significant role for other types of electrode materials.

Species rearrangement and proton transfer at electrolyte side

It is well recognized that the electrolyte in the electric double layer is quite different from the bulk one. Basically, ions with opposite charges and solvent molecules exhibit characteristic adsorption in the Helmholtz layer while waiting for further charge transfer.⁹⁶ However, the procedure between potential application and the start of the electrochemical reaction is quite a black box. A clear understanding of the specific structure and evolution of water molecules and ions at the electrode surface remains elusive.

Our group has provided a fundamental model to elucidate the interplay between ions, hydrated water, and H-bonds at the electrode/electrolyte interface.^{93,94} A framework was established that correlates the behavior of both experimentally observed and theoretically modeled water species at the interface. *In situ* Raman spectroscopy was used to monitor the evolution of water molecules at the interface with changing electrode potential. The results revealed a transformation of interfacial water from a random structure to a more ordered configuration composed of one-H-down and two-H-down configurations as the potential decreases (Figure 14C). Furthermore, the H-bond network at the interface also undergoes modifications. The intensities associated with 4-coordinated and 2-coordinated H-bonded water species decrease, while the signal corresponding to hydrated water with weaker H-bond increases. Density functional theory (DFT) calculations provided insights into the role of cations, which suggest the vibrational dipole moment of cation-water ligands (Na⁺·H₂O in our case) aligns more closely with the direction of the electric field compared to other water

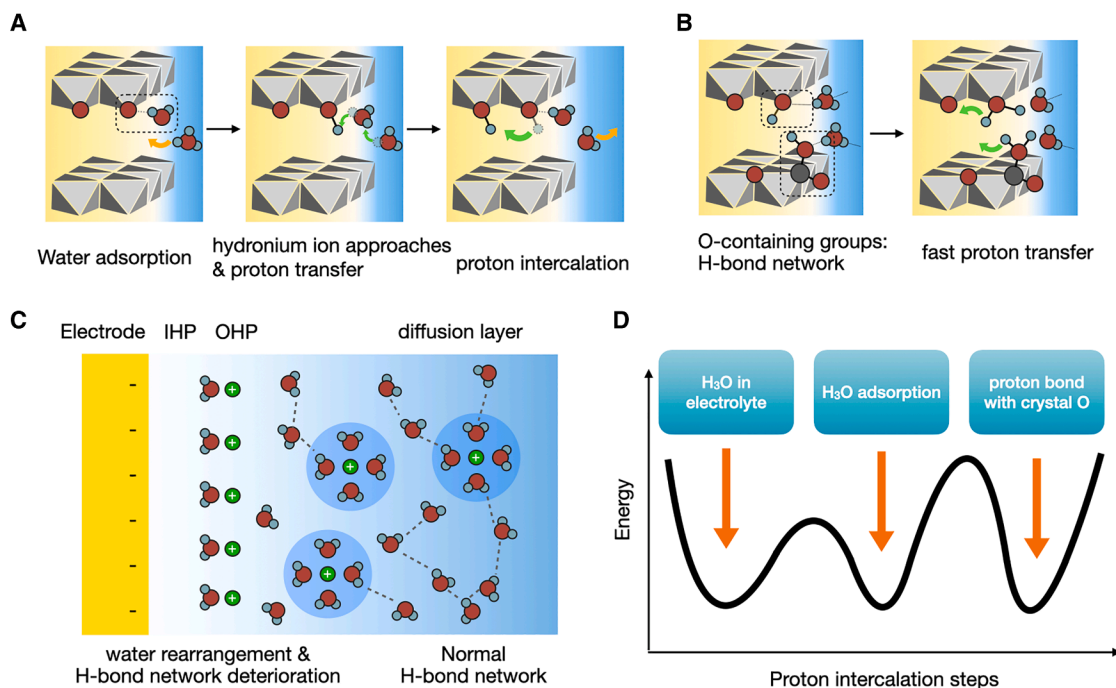


Figure 14. Proton transfer at the electrode/electrolyte interface

(A) Schematic diagram of surface reconstruction by water-based H-bond network.
 (B) Schematic diagram of surface reconstruction by plasma-induced H-bond network.
 (C) Electrolyte rearrangement and new H-bond-network generation in Helmholtz layer.⁹³
 (D) Energy consumption in proton-intercalation steps.⁹⁴

species. This alignment facilitates the transformation of ligands into the preferred two-H-down configuration at the interface. Consequently, hydrated water exhibits a closer proximity to the electrode surface compared to non-hydrated water molecules. In the experiment, the Na ions act as a co-catalyst in the Volmer step of HER by effective modification of H-bond network in the Helmholtz layer.

Furthermore, though not very clearly verified, we anticipate that protons should transfer differently in the new H-bond network. It can be rationalized by the fact that the two-H-down configuration may shorten the transfer path of protons and may facilitate further proton transfer from electrolyte to electrode surface. From this point of view, the proton transfer in electric double layers may be more efficient in metal-ion batteries. Since it is reported that the proton intercalation requires overcoming several energy barriers,⁹⁷ appropriated H-bond networks may accelerate proton transfer by lowering the energy barrier of H₂O adsorption (Figure 14D). Our work highlights the crucial role of cations in reconstructing the aqueous-battery interface at the electrolyte side. The findings demonstrate that hydrated water can generate more complex H-bond networks, and thus the proton transfer is heavily influenced.

CONCLUSIONS AND PERSPECTIVE

This review has comprehensively explored the multifaceted role of proton motion in aqueous batteries. Protons, the lightest charge carriers, leverage H-bond networks for efficient transfer

through a Grotthuss-type mechanism. This near-barrierless process facilitates rapid proton diffusion and high conductivity in electrode materials—a crucial advantage for aqueous batteries.

The focus of proton manipulation lies in strategically designing H-bond networks across electrodes, electrolytes, and interfaces. It broadens the range of electrode-material selection, making it possible to utilize low-price oxides of Mn, V, etc.

Solid electrodes can enable fast proton intercalation/deintercalation through consecutive H-bond networks formed by crystal water or pre-inserted water molecules. This approach has been successfully implemented in various aqueous-battery systems. Beyond traditional methods, we highlight a novel strategy for reinforcing H-bond networks through specific crystal defects such as structural distortions or vacancies. We note that, under appropriate structural configurations and O-site arrangements in oxides, inserted protons can generate new H-bond networks leading to promoted Grotthuss-like transport of subsequent protons. This structure-induced proton-transfer enhancement holds immense promise for the future design of high-performance proton-storage materials. Although this review mainly focuses on inorganic materials, we believe that the strategy is also suitable for organic candidates.⁹⁸

For electrolytes and interfaces, the situation becomes more nuanced. While faster proton transport enhances conductivity, it can also exacerbate detrimental side reactions such as OER and HER. Therefore, the optimization strategy often involves limiting proton movement by constraining water-based H-bond networks. This may appear counterintuitive at first glance;

however, it highlights the importance of striking a delicate balance between competing priorities in battery design—capacity, rate capability, and durability. One approach to achieve this balance involves incorporating organic additives with additional proton donor and/or acceptor sites. These additives can participate in the formation of new H-bond networks, replacing and hindering the original water-based networks. Alternatively, significantly reducing the water content can create a unique hydration shell around charge carriers and disrupt the continuity of water-based H-bond networks. Both methods can effectively impede proton motion, leading to slower interfacial side reactions.

The utilization of protons presents a compelling path forward for next-generation aqueous batteries. Their small size translates to high theoretical capacities for electrodes, while the Grotthuss-type transfer mechanism enables excellent rate performance. As discussed above, distinct H-bond network designs are crucial for optimizing electrodes and electrolytes in such systems. It is important to acknowledge that our understanding of proton motion remains incomplete. A recent study, for instance, revealed that proton transport can be mediated by atomic-scale non-flatness morphology in 2D membranes.⁹⁹ Such findings offer exciting possibilities for the future development of innovative proton-based batteries.

ACKNOWLEDGMENTS

This work was financially supported by the Basic and Applied Basic Research Foundation of Guangdong Province (2022A1515110446, 2023A1515011391 and 2021B1515130002), the National Natural Science Foundation of China (22109003), the Guangdong Key Laboratory of Design and Calculation of New Energy Materials (no. 2017B030301013), and the Major Science and Technology Infrastructure Project of Material Genome Big-science Facilities Platform supported by the Municipal Development and Reform Commission of Shenzhen.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

- Huang, K., Li, J., and Xu, Z. (2009). A novel process for recovering valuable metals from waste nickel-cadmium batteries. *Environ. Sci. Technol.* 43, 8974–8978. <https://doi.org/10.1021/es901659n>.
- Taniguchi, A., Fujioka, N., Ikoma, M., and Ohta, A. (2001). Development of nickel/metal-hydride batteries for EVs and HEVs. *J. Power Sources* 100, 117–124. [https://doi.org/10.1016/s0378-7753\(01\)00889-8](https://doi.org/10.1016/s0378-7753(01)00889-8).
- Lopes, P.P., and Stamenkovic, V.R. (2020). Past, present, and future of lead–acid batteries. *Science* 369, 923–924. <https://doi.org/10.1126/science.abd3352>.
- Liu, T., Lin, L., Bi, X., Tian, L., Yang, K., Liu, J., Li, M., Chen, Z., Lu, J., Amine, K., et al. (2019). In situ quantification of interphasial chemistry in Li-ion battery. *Nat. Nanotechnol.* 14, 50–56. <https://doi.org/10.1038/s41565-018-0284-y>.
- Chao, D., Zhou, W., Xie, F., Ye, C., Li, H., Jaroniec, M., and Qiao, S.-Z. (2020). Roadmap for advanced aqueous batteries: From design of materials to applications. *Sci. Adv.* 6, eaba4098. <https://doi.org/10.1126/sciadv.aba4098>.
- Zhong, C., Liu, B., Ding, J., Liu, X., Zhong, Y., Li, Y., Sun, C., Han, X., Deng, Y., Zhao, N., and Hu, W. (2020). Decoupling electrolytes towards stable and high-energy rechargeable aqueous zinc–manganese dioxide batteries. *Nat. Energy* 5, 440–449. <https://doi.org/10.1038/s41560-020-0584-y>.
- Jin, T., Ji, X., Wang, P.F., Zhu, K., Zhang, J., Cao, L., Chen, L., Cui, C., Deng, T., Liu, S., et al. (2021). High-Energy Aqueous Sodium-Ion Batteries. *Angew. Chem. Int. Ed.* 60, 11943–11948. <https://doi.org/10.1002/anie.202017167>.
- Shang, Y., and Kundu, D. (2023). A path forward for the translational development of aqueous zinc-ion batteries. *Joule* 7, 244–250. <https://doi.org/10.1016/j.joule.2023.01.011>.
- Xiao, X., Zhang, Z., Wu, Y., Xu, J., Gao, X., Xu, R., Huang, W., Ye, Y., Oyakhire, S.T., Zhang, P., et al. (2023). Ultrahigh-loading Manganese-based Electrode for Aqueous Battery via Polymorph Tuning. *Adv. Mater.* 35, 2211555. <https://doi.org/10.1002/adma.202211555>.
- Li, M., Wang, X., Meng, J., Zuo, C., Wu, B., Li, C., Sun, W., and Mai, L. (2024). Comprehensive Understandings of Hydrogen Bond Chemistry in Aqueous Batteries. *Adv. Mater.* 36, 2308628. <https://doi.org/10.1002/adma.202308628>.
- Wu, X., Hong, J.J., Shin, W., Ma, L., Liu, T., Bi, X., Yuan, Y., Qi, Y., Surta, T. W., Huang, W., et al. (2019). Diffusion-free Grotthuss topochemistry for high-rate and long-life proton batteries. *Nat. Energy* 4, 123–130. <https://doi.org/10.1038/s41560-018-0309-7>.
- Qin, R., Ding, S., Hou, C., Liu, L., Wang, Y., Zhao, W., Yao, L., Shao, Y., Zou, R., Zhao, Q., et al. (2023). Modulating the Proton-Conducting Lanes in Spinel ZnMn₂O₄ through Off-Stoichiometry. *Adv. Energy Mater.* 13, 2203915. <https://doi.org/10.1002/aenm.202203915>.
- Zhou, L., Liu, L., Hao, Z., Yan, Z., Yu, X.-F., Chu, P.K., Zhang, K., and Chen, J. (2021). Opportunities and challenges for aqueous metal-proton batteries. *Matter* 4, 1252–1273. <https://doi.org/10.1016/j.matt.2021.01.022>.
- Zhang, J., Chen, P., Yuan, B., Ji, W., Cheng, Z., and Qiu, X. (2013). Real-Space Identification of Intermolecular Bonding with Atomic Force Microscopy. *Science* 342, 611–614. <https://doi.org/10.1126/science.1242603>.
- Tian, Y., Hong, J., Cao, D., You, S., Song, Y., Cheng, B., Wang, Z., Guan, D., Liu, X., Zhao, Z., et al. (2022). Visualizing Eigen/Zundel cations and their interconversion in monolayer water on metal surfaces. *Science* 377, 315–319. <https://doi.org/10.1126/science.abo0823>.
- Lei, Y., Zhao, W., Yin, J., Ma, Y., Zhao, Z., Yin, J., Khan, Y., Hedhili, M.N., Chen, L., Wang, Q., et al. (2023). Discovery of a three-proton insertion mechanism in α -molybdenum trioxide leading to enhanced charge storage capacity. *Nat. Commun.* 14, 5490. <https://doi.org/10.1038/s41467-023-41277-8>.
- Makivić, N., Cho, J.-Y., Harris, K.D., Tarascon, J.-M., Limoges, B., and Baland, V. (2021). Evidence of Bulk Proton Insertion in Nanostructured Anatase and Amorphous TiO₂ Electrodes. *Chem. Mater.* 33, 3436–3448. <https://doi.org/10.1021/acs.chemmater.1c00840>.
- Liu, T., Liu, J., Li, L., Yu, L., Diao, J., Zhou, T., Li, S., Dai, A., Zhao, W., Xu, S., et al. (2022). Origin of structural degradation in Li-rich layered oxide cathode. *Nature* 606, 305–312. <https://doi.org/10.1038/s41586-022-04689-y>.
- Usiskin, R., Lu, Y., Popovic, J., Law, M., Balaya, P., Hu, Y.-S., and Maier, J. (2021). Fundamentals, status and promise of sodium-based batteries. *Nat. Rev. Mater.* 6, 1020–1035. <https://doi.org/10.1038/s41578-021-00324-w>.
- Manthiram, A., and Goodenough, J.B. (2021). Layered lithium cobalt oxide cathodes. *Nat. Energy* 6, 323. <https://doi.org/10.1038/s41560-020-00764-8>.
- Shi, B., Pang, X., Li, S., Wu, H., Shen, J., Wang, X., Fan, C., Cao, L., Zhu, T., Qiu, M., et al. (2022). Short hydrogen-bond network confined on COF surfaces enables ultrahigh proton conductivity. *Nat. Commun.* 13, 6666. <https://doi.org/10.1038/s41467-022-33868-8>.
- Odendahl, N.L., and Geissler, P.L. (2022). Local Ice-like Structure at the Liquid Water Surface. *J. Am. Chem. Soc.* 144, 11178–11188. <https://doi.org/10.1021/jacs.2c01827>.

23. Tang, F., Li, Z., Zhang, C., Louie, S.G., Car, R., Qiu, D.Y., and Wu, X. (2022). Many-body effects in the X-ray absorption spectra of liquid water. *Proc. Natl. Acad. Sci. USA* 119, e2201258119. <https://doi.org/10.1073/pnas.2201258119>.
24. Park, K., Lin, W., and Paesani, F. (2014). Fast and Slow Proton Transfer in Ice: The Role of the Quasi-Liquid Layer and Hydrogen-Bond Network. *J. Phys. Chem. B* 118, 8081–8089. <https://doi.org/10.1021/jp501116d>.
25. Kennedy, D., and Norman, C. (2005). What Don't We Know? *Science* 309, 75. <https://doi.org/10.1126/science.309.5731.75>.
26. Kreuer, K.-D. (1996). Proton Conductivity: Materials and Applications. *Chem. Mater.* 8, 610–641. <https://doi.org/10.1021/cm950192a>.
27. Miyake, T., and Rolandi, M. (2016). Grotthuss mechanisms: from proton transport in proton wires to bioprotonic devices. *J. Phys. Condens. Matter* 28, 023001. <https://doi.org/10.1088/0953-8984/28/2/023001>.
28. Ekimova, M., Kleine, C., Ludwig, J., Ochmann, M., Agrenius, T.E.G., Kozari, E., Pines, D., Pines, E., Huse, N., Wernet, P., et al. (2022). From Local Covalent Bonding to Extended Electric Field Interactions in Proton Hydration. *Angew. Chem. Int. Ed.* 61, e202211066. <https://doi.org/10.1002/anie.202211066>.
29. Kim, Y., Shin, S., and Kang, H. (2015). Zundel-like and Eigen-like Hydrated Protons on a Platinum Surface. *Angew. Chem. Int. Ed.* 54, 7626–7630. <https://doi.org/10.1002/anie.201500410>.
30. Kreuer, K., Rabenau, A., and Weppner, W. (1982). Vehicle Mechanism, A New Model for the Interpretation of the Conductivity of Fast Proton Conductors. *Angew. Chem. Int. Ed.* 21, 208–209. <https://doi.org/10.1002/anie.198202082>.
31. Zhang, Q., Zhang, J., Qiu, J., Chen, C., Yang, Z., Li, W., Wang, M., Li, T., Wu, W., and Wang, J. (2024). Detecting the Conduction Property of Proton Carriers at Different Relative Humidity Based on Postsynthetic MOF Nanosheets. *ACS Appl. Mater. Interfaces* 16, 67697–67705. <https://doi.org/10.1021/acsami.4c13776>.
32. Park, M.J., Yaghoobnejad Asl, H., and Manthiram, A. (2020). Multivalent-Ion versus Proton Insertion into Battery Electrodes. *ACS Energy Lett.* 5, 2367–2375. <https://doi.org/10.1021/acsenenergylett.0c01021>.
33. Shu, Q., Chen, L., Xia, Y., Gong, X., and Gu, X. (2013). Proton-Induced Dysfunction Mechanism of Cathodes in an Aqueous Lithium Ion Battery. *J. Phys. Chem. C* 117, 6929–6932. <https://doi.org/10.1021/jp311270s>.
34. Hu, X., Zhang, W., Liu, X., Mei, Y., and Huang, Y. (2015). Nanostructured Mo-based electrode materials for electrochemical energy storage. *Chem. Soc. Rev.* 44, 2376–2404. <https://doi.org/10.1039/c4cs00350k>.
35. Guo, H., Goonetilleke, D., Sharma, N., Ren, W., Su, Z., Rawal, A., and Zhao, C. (2020). Two-Phase Electrochemical Proton Transport and Storage in α -MoO₃ for Proton Batteries. *Cell Rep. Phys. Sci.* 1, 100225. <https://doi.org/10.1016/j.xcrp.2020.100225>.
36. Zhao, Q., Liu, L., Yin, J., Zheng, J., Zhang, D., Chen, J., and Archer, L.A. (2020). Proton Intercalation/De-Intercalation Dynamics in Vanadium Oxides for Aqueous Aluminum Electrochemical Cells. *Angew. Chem. Int. Ed.* 59, 3048–3052. <https://doi.org/10.1002/anie.201912634>.
37. Wang, Y., Chen, C., Ren, H., Qin, R., Yi, H., Ding, S., Li, Y., Yao, L., Li, S., Zhao, Q., and Pan, F. (2021). Superior cycling stability of H_{0.642}V₂O₅·0.143H₂O in rechargeable aqueous zinc batteries. *Sci. China Mater.* 65, 78–84. <https://doi.org/10.1007/s40843-021-1730-1>.
38. Yi, H., Zuo, C., Ren, H., Zhao, W., Wang, Y., Ding, S., Li, Y., Qin, R., Zhou, L., Yao, L., et al. (2021). Structure evolution and energy storage mechanism of Zn₃V₃O₈ spinel in aqueous zinc batteries. *Nanoscale* 13, 14408–14416. <https://doi.org/10.1039/d1nr02347k>.
39. Zhao, Y., Ouyang, M., Wang, Y., Qin, R., Zhang, H., Pan, W., Leung, D.Y.C., Wu, B., Liu, X., Brandon, N.P., et al. (2022). Biomimetic Lipid-Bilayer Anode Protection for Long Lifetime Aqueous Zinc-Metal Batteries. *Adv. Funct. Mater.* 32. <https://doi.org/10.1002/adfm.202203019>.
40. Yuan, Y., Sharpe, R., He, K., Li, C., Saray, M.T., Liu, T., Yao, W., Cheng, M., Jin, H., Wang, S., et al. (2022). Understanding intercalation chemistry for sustainable aqueous zinc–manganese dioxide batteries. *Nat. Sustain.* 5, 890–898. <https://doi.org/10.1038/s41893-022-00919-3>.
41. Xu, C., Li, B., Du, H., and Kang, F. (2012). Energetic zinc ion chemistry: the rechargeable zinc ion battery. *Angew. Chem. Int. Ed.* 51, 933–935. <https://doi.org/10.1002/anie.201106307>.
42. Liu, L., Ding, S., Yao, L., Liu, M., Li, S., Zhao, Q., Qin, R., and Pan, F. (2023). *In situ* BaSO₄ coating enabled activation-free and ultra-stable δ -MnO₂ for aqueous Zn-ion batteries. *Chem. Commun.* 59, 6227–6230. <https://doi.org/10.1039/d3cc01086d>.
43. Pan, H., Shao, Y., Yan, P., Cheng, Y., Han, K.S., Nie, Z., Wang, C., Yang, J., Li, X., Bhattacharya, P., et al. (2016). Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. *Nat. Energy* 1, 16039. <https://doi.org/10.1038/nenergy.2016.39>.
44. Zhao, Q., Chen, X., Wang, Z., Yang, L., Qin, R., Yang, J., Song, Y., Ding, S., Weng, M., Huang, W., et al. (2019). Unravelling H⁺/Zn²⁺ Synergistic Intercalation in a Novel Phase of Manganese Oxide for High-Performance Aqueous Rechargeable Battery. *Small* 15, 1904545. <https://doi.org/10.1002/sml.201904545>.
45. Ding, S., Zhang, M., Qin, R., Fang, J., Ren, H., Yi, H., Liu, L., Zhao, W., Li, Y., Yao, L., et al. (2021). Oxygen-Deficient β -MnO₂@Graphene Oxide Cathode for High-Rate and Long-Life Aqueous Zinc Ion Batteries. *Nano-Micro Lett.* 13, 173. <https://doi.org/10.1007/s40820-021-00691-7>.
46. Zhao, Q., Song, A., Zhao, W., Qin, R., Ding, S., Chen, X., Song, Y., Yang, L., Lin, H., Li, S., and Pan, F. (2021). Boosting the Energy Density of Aqueous Batteries via Facile Grotthuss Proton Transport. *Angew. Chem. Int. Ed.* 60, 4169–4174. <https://doi.org/10.1002/anie.202011588>.
47. Huang, M., He, Q., Wang, J., Liu, X., Xiong, F., Liu, Y., Guo, R., Zhao, Y., Yang, J., and Mai, L. (2023). NH₄⁺ Deprotonation at Interfaces Induced Reversible H₃O⁺/NH₄⁺ Co-insertion/Extraction. *Angew. Chem. Int. Ed.* 62, e202218922. <https://doi.org/10.1002/anie.202218922>.
48. Yi, H., Qin, R., Ding, S., Wang, Y., Li, S., Zhao, Q., and Pan, F. (2021). Structure and Properties of Prussian Blue Analogues in Energy Storage and Conversion Applications. *Adv. Funct. Mater.* 31, 2006970. <https://doi.org/10.1002/adfm.202006970>.
49. Simonov, A., De Baerdemaeker, T., Boström, H.L.B., Gómez, M.L.R., Gray, H.J., Chernyshov, D., Bosak, A., Bürgi, H.-B., and Goodwin, A.L. (2020). Hidden diversity of vacancy networks in Prussian blue analogues. *Nature* 578, 256–260. <https://doi.org/10.1038/s41586-020-1980-y>.
50. Xie, Z.-L., Zhu, Y., Du, J.-Y., Yang, D.-Y., Zhang, N., Sun, Q.-Q., Huang, G., and Zhang, X.B. (2024). Reconfiguring the Hydrogen Networks of Aqueous Electrolyte to Stabilize Iron Hexacyanoferrate for High-Voltage pH-Decoupled Cell. *Angew. Chem. Int. Ed.* 63, e202400916. <https://doi.org/10.1002/anie.202400916>.
51. Peng, X., Guo, H., Ren, W., Su, Z., and Zhao, C. (2020). Vanadium hexacyanoferrate as high-capacity cathode for fast proton storage. *Chem. Commun.* 56, 11803–11806. <https://doi.org/10.1039/d0cc03974h>.
52. Chen, Z., Peng, Y., Liu, F., Le, Z., Zhu, J., Shen, G., Zhang, D., Wen, M., Xiao, S., Liu, C.-P., et al. (2015). Hierarchical Nanostructured WO₃ with Biomimetic Proton Channels and Mixed Ionic-Electronic Conductivity for Electrochemical Energy Storage. *Nano Lett.* 15, 6802–6808. <https://doi.org/10.1021/acs.nanolett.5b02642>.
53. Mitchell, J.B., Geise, N.R., Paterson, A.R., Osti, N.C., Sun, Y., Fleischmann, S., Zhang, R., Madsen, L.A., Toney, M.F., Jiang, D.e., et al. (2019). Confined Interlayer Water Promotes Structural Stability for High-Rate Electrochemical Proton Intercalation in Tungsten Oxide Hydrates. *ACS Energy Lett.* 4, 2805–2812. <https://doi.org/10.1021/acsenenergylett.9b02040>.
54. Lin, H., Zhou, F., Liu, C.-P., and Ozoliņš, V. (2014). Non-Grotthuss proton diffusion mechanism in tungsten oxide dihydrate from first-principles calculations. *J. Mater. Chem. A* 2, 12280–12288. <https://doi.org/10.1039/c4ta02465f>.
55. Jiang, H., Hong, J.J., Wu, X., Surta, T.W., Qi, Y., Dong, S., Li, Z., Leonard, D.P., Holoubek, J.J., Wong, J.C., et al. (2018). Insights on the Proton

- Insertion Mechanism in the Electrode of Hexagonal Tungsten Oxide Hydrate. *J. Am. Chem. Soc.* **140**, 11556–11559. <https://doi.org/10.1021/jacs.8b03959>.
56. Lukatskaya, M.R., Kota, S., Lin, Z., Zhao, M.-Q., Shpigol, N., Levi, M.D., Halim, J., Taberna, P.-L., Barsoum, M.W., Simon, P., and Gogotsi, Y. (2017). Ultra-high-rate pseudocapacitive energy storage in two-dimensional transition metal carbides. *Nat. Energy* **2**, 17105. <https://doi.org/10.1038/nenergy.2017.105>.
57. Sun, Y., Zhan, C., Kent, P.R.C., Naguib, M., Gogotsi, Y., and Jiang, D.E. (2020). Proton Redox and Transport in MXene-Confined Water. *ACS Appl. Mater. Interfaces* **12**, 763–770. <https://doi.org/10.1021/acsami.9b18139>.
58. Shao, H., Xu, K., Wu, Y.-C., Iadecola, A., Liu, L., Ma, H., Qu, L., Raymundo-Piñero, E., Zhu, J., Lin, Z., et al. (2020). Unraveling the Charge Storage Mechanism of $\text{Ti}_3\text{C}_2\text{Tx}$ MXene Electrode in Acidic Electrolyte. *ACS Energy Lett.* **5**, 2873–2880. <https://doi.org/10.1021/acsenenergylett.0c01290>.
59. Wen, J., Fu, Q., Wu, W., Gao, H., Zhang, X., and Wang, B. (2019). Understanding the Different Diffusion Mechanisms of Hydrated Protons and Potassium Ions in Titanium Carbide MXene. *ACS Appl. Mater. Interfaces* **11**, 7087–7095. <https://doi.org/10.1021/acsami.8b21117>.
60. Yu, M., Shao, H., Wang, G., Yang, F., Liang, C., Rozier, P., Wang, C.-Z., Lu, X., Simon, P., and Feng, X. (2020). Interlayer gap widened α -phase molybdenum trioxide as high-rate anodes for dual-ion-intercalation energy storage devices. *Nat. Commun.* **11**, 1348. <https://doi.org/10.1038/s41467-020-15216-w>.
61. Wang, X., Xie, Y., Tang, K., Wang, C., and Yan, C. (2018). Redox Chemistry of Molybdenum Trioxide for Ultrafast Hydrogen-Ion Storage. *Angew. Chem. Int. Ed.* **57**, 11569–11573. <https://doi.org/10.1002/anie.201803664>.
62. Xu, W., Zhao, K., Liao, X., Sun, C., He, K., Yuan, Y., Ren, W., Li, J., Li, T., Yang, C., et al. (2022). Proton Storage in Metallic $\text{H}_{1.75}\text{MoO}_3$ Nanobelts through the Grotthuss Mechanism. *J. Am. Chem. Soc.* **144**, 17407–17415. <https://doi.org/10.1021/jacs.2c03844>.
63. Ma, Z., Shi, X.-M., Nishimura, S.-I., Ko, S., Okubo, M., and Yamada, A. (2022). Anhydrous Fast Proton Transport Boosted by the Hydrogen Bond Network in a Dense Oxide-Ion Array of α - MoO_3 . *Adv. Mater.* **34**, e2203335. <https://doi.org/10.1002/adma.202203335>.
64. Zhao, H., Fu, Q., Yang, D., Sarapulova, A., Pang, Q., Meng, Y., Wei, L., Ehrenberg, H., Wei, Y., Wang, C., and Chen, G. (2020). *In Operando* Synchrotron Studies of NH_4^+ Preintercalated $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ Nanobelts as the Cathode Material for Aqueous Rechargeable Zinc Batteries. *ACS Nano* **14**, 11809–11820. <https://doi.org/10.1021/acsnano.0c04669>.
65. Li, M., Zhang, Y., Hu, J., Wang, X., Zhu, J., Niu, C., Han, C., and Mai, L. (2022). Universal multifunctional hydrogen bond network construction strategy for enhanced aqueous Zn^{2+} /proton hybrid batteries. *Nano Energy* **100**, 107539. <https://doi.org/10.1016/j.nanoen.2022.107539>.
66. Shen, X., Wang, X., Zhou, Y., Shi, Y., Zhao, L., Jin, H., Di, J., and Li, Q. (2021). Highly Reversible Aqueous Zn-MnO₂ Battery by Supplementing Mn^{2+} -Mediated MnO_2 Deposition and Dissolution. *Adv. Funct. Mater.* **31**, 2101579. <https://doi.org/10.1002/adfm.202101579>.
67. Ivanov, A.A. (2008). Electrical conductivity of aqueous acids in binary and ternary water-electrolyte systems. *Russ. J. Inorg. Chem.* **53**, 1948–1963. <https://doi.org/10.1134/s003602360812019x>.
68. Fournier, J.A., Carpenter, W.B., Lewis, N.H.C., and Tokmakoff, A. (2018). Broadband 2D IR spectroscopy reveals dominant asymmetric H_5O_2^+ proton hydration structures in acid solutions. *Nat. Chem.* **10**, 932–937. <https://doi.org/10.1038/s41557-018-0091-y>.
69. Calio, P.B., Li, C., and Voth, G.A. (2021). Resolving the Structural Debate for the Hydrated Excess Proton in Water. *J. Am. Chem. Soc.* **143**, 18672–18683. <https://doi.org/10.1021/jacs.1c08552>.
70. Dahms, F., Fingerhut, B.P., Nibbering, E.T.J., Pines, E., and Elsaesser, T. (2017). Large-amplitude transfer motion of hydrated excess protons mapped by ultrafast 2D IR spectroscopy. *Science* **357**, 491–495. <https://doi.org/10.1126/science.aan5144>.
71. Jiang, H., Shin, W., Ma, L., Hong, J.J., Wei, Z., Liu, Y., Zhang, S., Wu, X., Xu, Y., Guo, Q., et al. (2020). A High-Rate Aqueous Proton Battery Delivering Power Below -78°C via an Unfrozen Phosphoric Acid. *Adv. Energy Mater.* **10**, 2000968. <https://doi.org/10.1002/aenm.202000968>.
72. Vilčiauskas, L., Tuckerman, M.E., Bester, G., Paddison, S.J., and Kreuer, K.-D. (2012). The mechanism of proton conduction in phosphoric acid. *Nat. Chem.* **4**, 461–466. <https://doi.org/10.1038/nchem.1329>.
73. Popov, I., Zhu, Z., Young-Gonzales, A.R., Sacchi, R.L., Mamontov, E., Gainaru, C., Paddison, S.J., and Sokolov, A.P. (2023). Search for a Grotthuss mechanism through the observation of proton transfer. *Commun. Chem.* **6**, 77. <https://doi.org/10.1038/s42004-023-00878-6>.
74. Sui, Y., and Ji, X. (2021). Anticatalytic Strategies to Suppress Water Electrolysis in Aqueous Batteries. *Chem. Rev.* **121**, 6654–6695. <https://doi.org/10.1021/acs.chemrev.1c00191>.
75. Xie, J., Liang, Z., and Lu, Y.-C. (2020). Molecular crowding electrolytes for high-voltage aqueous batteries. *Nat. Mater.* **19**, 1006–1011. <https://doi.org/10.1038/s41563-020-0667-y>.
76. Wang, S., Jiang, H., Dong, Y., Clarkson, D., Zhu, H., Settens, C.M., Ren, Y., Nguyen, T., Han, F., Fan, W., et al. (2022). Acid-in-Clay Electrolyte for Wide-Temperature-Range and Long-Cycle Proton Batteries. *Adv. Mater.* **34**, 2202063. <https://doi.org/10.1002/adma.202202063>.
77. Zhang, Y., Zhu, M., Wu, K., Yu, F., Wang, G., Xu, G., Wu, M., Liu, H.-K., Dou, S.-X., and Wu, C. (2021). An in-depth insight of a highly reversible and dendrite-free Zn metal anode in an hybrid electrolyte. *J. Mater. Chem. A* **9**, 4253–4261. <https://doi.org/10.1039/d0ta11668h>.
78. Wang, K., Qiu, T., Lin, L., Liu, F., Zhu, J., Liu, X.-X., and Sun, X. (2023). Interface solvation regulation stabilizing the Zn metal anode in aqueous Zn batteries. *Chem. Sci.* **14**, 8076–8083. <https://doi.org/10.1039/d3sc01831h>.
79. Li, T.C., Lin, C., Luo, M., Wang, P., Li, D.-S., Li, S., Zhou, J., and Yang, H.Y. (2023). Interfacial Molecule Engineering for Reversible Zn Electrochemistry. *ACS Energy Lett.* **8**, 3258–3268. <https://doi.org/10.1021/acsenenergylett.3c00859>.
80. Sun, P., Ma, L., Zhou, W., Qiu, M., Wang, Z., Chao, D., and Mai, W. (2021). Simultaneous Regulation on Solvation Shell and Electrode Interface for Dendrite-Free Zn Ion Batteries: Achieved by a Low-Cost Glucose Additive. *Angew. Chem. Int. Ed.* **60**, 18247–18255. <https://doi.org/10.1002/anie.202105756>.
81. Qin, R., Wang, Y., Zhang, M., Wang, Y., Ding, S., Song, A., Yi, H., Yang, L., Song, Y., Cui, Y., et al. (2021). Tuning Zn^{2+} coordination environment to suppress dendrite formation for high-performance Zn-ion batteries. *Nano Energy* **80**, 105478. <https://doi.org/10.1016/j.nanoen.2020.105478>.
82. Xu, D., Ren, X., Li, H., Zhou, Y., Chai, S., Chen, Y., Li, H., Bai, L., Chang, Z., Pan, A., and Zhou, H. (2024). Chelating Additive Regulating Zn-Ion Solvation Chemistry for Highly Efficient Aqueous Zinc-Metal Battery. *Angew. Chem. Int. Ed.* **63**, e202402833. <https://doi.org/10.1002/anie.202402833>.
83. Wang, Y., Yang, L., Xu, P., Liu, L., Li, S., Zhao, Y., Qin, R., and Pan, F. (2024). An Electrochemically Initiated Self-Limiting Hydrogel Electrolyte for Dendrite-Free Zinc Anode. *Small* **20**, 2307446. <https://doi.org/10.1002/smll.202307446>.
84. Suo, L., Borodin, O., Gao, T., Olguin, M., Ho, J., Fan, X., Luo, C., Wang, C., and Xu, K. (2015). “Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* **350**, 938–943. <https://doi.org/10.1126/science.aab1595>.
85. Yang, C., Xia, J., Cui, C., Pollard, T.P., Vatamanu, J., Faraone, A., Dura, J. A., Tyagi, M., Kattan, A., Thimsen, E., et al. (2023). All-temperature zinc batteries with high-entropy aqueous electrolyte. *Nat. Sustain.* **6**, 325–335. <https://doi.org/10.1038/s41893-022-01028-x>.
86. Jiang, H., Tang, L., Fu, Y., Wang, S., Sandstrom, S.K., Scida, A.M., Li, G., Hoang, D., Hong, J.J., Chiu, N.-C., et al. (2023). Chloride electrolyte enabled practical zinc metal battery with a near-unity Coulombic

- efficiency. *Nat. Sustain.* 6, 806–815. <https://doi.org/10.1038/s41893-023-01092-x>.
87. Wang, Y., Wang, T., Dong, D., Xie, J., Guan, Y., Huang, Y., Fan, J., and Lu, Y.-C. (2022). Enabling high-energy-density aqueous batteries with hydrogen bond-anchored electrolytes. *Matter* 5, 162–179. <https://doi.org/10.1016/j.matt.2021.10.021>.
88. Dong, D., Xie, J., Liang, Z., and Lu, Y.-C. (2022). Tuning Intermolecular Interactions of Molecular Crowding Electrolyte for High-Performance Aqueous Batteries. *ACS Energy Lett.* 7, 123–130. <https://doi.org/10.1021/acsenergylett.1c02064>.
89. Zheng, J., Tan, G., Shan, P., Liu, T., Hu, J., Feng, Y., Yang, L., Zhang, M., Chen, Z., Lin, Y., et al. (2018). Understanding Thermodynamic and Kinetic Contributions in Expanding the Stability Window of Aqueous Electrolytes. *Chem* 4, 2872–2882. <https://doi.org/10.1016/j.chempr.2018.09.004>.
90. Roget, S.A., Carter-Fenk, K.A., and Fayer, M.D. (2022). Water Dynamics and Structure of Highly Concentrated LiCl Solutions Investigated Using Ultrafast Infrared Spectroscopy. *J. Am. Chem. Soc.* 144, 4233–4243. <https://doi.org/10.1021/jacs.2c00616>.
91. Qin, R., Wang, Y., Yao, L., Yang, L., Zhao, Q., Ding, S., Liu, L., and Pan, F. (2022). Progress in interface structure and modification of zinc anode for aqueous batteries. *Nano Energy* 98, 107333. <https://doi.org/10.1016/j.nanoen.2022.107333>.
92. Zheng, J., Hou, Y., Duan, Y., Song, X., Wei, Y., Liu, T., Hu, J., Guo, H., Zhuo, Z., Liu, L., et al. (2015). Janus Solid–Liquid Interface Enabling Ultra-high Charging and Discharging Rate for Advanced Lithium-Ion Batteries. *Nano Lett.* 15, 6102–6109. <https://doi.org/10.1021/acs.nanolett.5b02379>.
93. Wang, Y.-H., Zheng, S., Yang, W.-M., Zhou, R.-Y., He, Q.-F., Radjenovic, P., Dong, J.-C., Li, S., Zheng, J., Yang, Z.-L., et al. (2021). In situ Raman spectroscopy reveals the structure and dissociation of interfacial water. *Nature* 600, 81–85. <https://doi.org/10.1038/s41586-021-04068-z>.
94. Wang, Y.-H., Li, S., Zhou, R.-Y., Zheng, S., Zhang, Y.-J., Dong, J.-C., Yang, Z.-L., Pan, F., Tian, Z.-Q., and Li, J.-F. (2023). In situ electrochemical Raman spectroscopy and ab initio molecular dynamics study of interfacial water on a single-crystal surface. *Nat. Protoc.* 18, 883–901. <https://doi.org/10.1038/s41596-022-00782-8>.
95. Zhang, J., Fu, K., Du, K., Wen, C., Yu, J., Han, C., Hu, Y., and Xu, L. (2024). Realizing a Mildly Acidic Proton Battery via Surface Functionalization. *ACS Energy Lett.* 9, 1853–1862. <https://doi.org/10.1021/acsenergylett.3c02571>.
96. Cao, L., Li, D., Pollard, T., Deng, T., Zhang, B., Yang, C., Chen, L., Vatanmanu, J., Hu, E., Hourwitz, M.J., et al. (2021). Fluorinated interphase enables reversible aqueous zinc battery chemistries. *Nat. Nanotechnol.* 16, 902–910. <https://doi.org/10.1038/s41565-021-00905-4>.
97. Grifoni, E., Piccini, G., Lercher, J.A., Glezakou, V.-A., Rousseau, R., and Parrinello, M. (2021). Confinement effects and acid strength in zeolites. *Nat. Commun.* 12, 2630. <https://doi.org/10.1038/s41467-021-22936-0>.
98. Wu, Z., Yang, P., Wang, S., Li, S., and Zhang, S. (2022). Emerging organic electrode materials for aqueous proton batteries. *Trends Chem.* 4, 1121–1134. <https://doi.org/10.1016/j.trechm.2022.09.007>.
99. Wahab, O.J., Daviddi, E., Xin, B., Sun, P.Z., Griffin, E., Colburn, A.W., Barry, D., Yagmurcukardes, M., Peeters, F.M., Geim, A.K., et al. (2023). Proton transport through nanoscale corrugations in two-dimensional crystals. *Nature* 620, 782–786. <https://doi.org/10.1038/s41586-023-06247-6>.