Diffusion-free Grotthuss topochemistry for high-rate and long-life proton batteries

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The design of Faradaic battery electrodes that exhibit high rate capability and long cycle life equivalent to those of the electrodes of electrical double-layer capacitors is a big challenge. Here we report a strategy to fill this performance gap using the concept of Grotthuss proton conduction, in which proton transfer takes place by means of concerted cleavage and formation of O–H bonds in a hydrogen-bonding network. We show that in a hydrated Prussian blue analogue (Turnbull’s blue) the abundant lattice water molecules with a contiguous hydrogen-bonding network facilitate Grotthuss proton conduction during redox reactions. When using it as a battery electrode, we find high-rate behaviours at 4,000 C (380 A g⁻¹, 508 mA cm⁻²), and a long cycling life of 0.73 million cycles. These results for diffusion-free Grotthuss topochemistry of protons, in contrast to orthodox battery electrochemistry, which requires ion diffusion inside electrodes, indicate a potential direction to revolutionize electrochemical energy storage for high-power applications.

Faradaic electrodes that possess the high capacity of batteries, while simultaneously delivering the high rate capability and excellent cycle life of electrodes in electrical double-layer capacitors, represent a grand challenge for electrochemical energy storage, and a class of such materials would transform our use of electrical energy. The rate performance of Faradaic electrodes is partially governed by transportation of ion charge carriers inside electrodes, which in turn depends on the choice of ion charge carriers. So far, most attention has been devoted to devices operating on metal ions, starting with Li and looking down the periodic table. Relatively little consideration has been given to looking up the periodic table to hydrogen, despite the hydrogen ion—a single proton—being much smaller than any metal ion. In addition to its advantage of size, the presence of hydrogen as a constituent of water enables fast conduction of protons in aqueous systems by a diffusional mechanism first postulated by von Grotthuss in 1806. In this process, shown in Fig. 1a, an H atom bridging two molecules to the other, kicking out one of the existing H atoms from its adopted molecule, and triggering a chain of similar displacements through the hydrogen-bonding network. The motion is akin to a Newton’s cradle (Fig. 1b), with correlated local displacements leading to long-range transport of protons—very different from conduction of metal ions, where solvated metal ions diffuse long distances individually. Grotthuss proton conduction is very fast, and it is responsible for the anomalously high conductivity of acids. Recent studies have suggested that Grotthuss conduction may also take place in hydrogen-bonding networks confined inside solids, such as hydrated metal–organic frameworks. However, it has thus far remained unknown whether Grotthuss conduction can facilitate the redox reactions in battery electrodes to enable a high rate capability for electrochemical devices.

Herein, we report an electrode material—a defective Prussian blue analogue (PBA), more specifically a Turnbull’s blue analogue (TBA), Cu[Fe(CN)₆]₀·₆·3.₄·H₂O (CuFe-TBA), where □ represents a ferri-cyanide vacancy; this material explicitly plays out the benefits of Grotthuss proton conduction on the rate and cycling performance of a Faradaic electrode. At the extremely high charging rate of 4,000 C (380 A g⁻¹, 508 mA cm⁻²), the CuFe-TBA electrode retains half the capacity obtained at 1 C (1 C is defined as 95 mA g⁻¹)—rivaling the fastest electrodes in any electrochemical storage device. Furthermore, CuFe-TBA maintains 60% of its capacity after 0.73 million cycles at 500 C, the largest number of cycles ever reported for a Faradaic electrode. The CuFe-TBA electrode uses protons as its working ions, providing a fast charge transport mechanism not available to traditional metal–ion batteries. Synchrotron X-ray and neutron diffraction measurements, combined with the first-principles calculations, show that the superlative performance of CuFe-TBA originates from its contiguous network of hydrogen-bonded lattice water, which mediates Grotthuss proton conduction. Taking advantage of Grotthuss topochemistry engenders an exciting avenue for bridging the performance gap between capacitors and batteries.

Crystal structures and electrochemical performance of PBAs

We aim to design electrode materials that harness Grotthuss proton conduction to deliver exceptional power density of batteries. A TBA, Cu[Fe(CN)₆]₀·₆·3.₄·H₂O (CuFe-TBA), was selected as a model electrode; it operates in an acidic aqueous electrolyte and has an open framework architecture filled with a crystal water network. TBAs with the specific stoichiometry Mₓ[Fe⁴⁺(CN)₆]₀·₆·3·H₂O are a subset of the well-known family of PBAs, where M is a transition metal. Besides TBA, there are another two classes of PBAs that differ in their vacancies stoichiometry: Berlin...
Mit appears that the 2.0 M H₂SO₄ electrolyte renders the rate performance of CuFe-TBA optimal in comparison with other concentrations (Supplementary Fig. 4). Additionally, primarily on the basis of its superior cycling stability compared with other MFe-TBA compounds (Supplementary Fig. 4). This capacity corresponds to Feiii/Feii₃₂,₃₅. This contrasts with the two-redox-pair behaviour of the electrode to be charged and discharged to near its theoretical capacity at unprecedented rates, and for hundreds of thousands of cycles. CuFe-TBA was synthesized by aqueous precipitation, and the results of its basic characterization are shown in Supplementary Table 1 and Supplementary Figs. 1–3. Galvanostatic charge/discharge (GCD) measurements of CuFe-TBA in 2.0 M H₂SO₄ electrolyte showed a reversible capacity of 95 mAh g⁻¹ (0.14 mAh cm⁻²) when discharged at a current rate of 1 C. This capacity corresponds to the storage of 0.91 protons per Cu[Fe(CN)]₆[3.4H₂O formula unit, thus all the Fe⁰ is reduced to Fe⁰, and 28% Cu⁰ is converted to Cu⁰ (refs. ₃₂,₃₅). We selected CuFe-TBA as the model compound primarily on the basis of its superior cycling stability compared with other MFe-TBA compounds (Supplementary Fig. 4). Additionally, it appears that the 2.0 M H₂SO₄ electrolyte renders the rate performance of CuFe-TBA optimal in comparison with other concentrations (Supplementary Fig. 4).

To study the rate performance of CuFe-TBA, GCD curves recorded at 20 C, 200 C, 2,000 C and 4,000 C show corresponding capacities of 78, 67, 56 and 49 mAh g⁻¹, respectively (Fig. 2a). At 4,000 C, CuFe-TBA discharges in just 0.46 s, but retains half of its 1 C capacity. It is notable in Fig. 2a that the potential hysteresis (polarization) between the charge and discharge profiles increases linearly with the current rate, suggesting that the rate performance of CuFe-TBA is limited more by the testing cells’ electrical resistance than the proton transport and the reaction kinetics. Such rate performance is comparable with the fastest electrodes in electrical double-layer capacitors, and exceeds the high rate performance of most other Faradaic electrodes (see comparison in Supplementary Fig. 5). The electrochemical performance of CuFe-TBA is robust both to increasing the active mass loading (see Supplementary Fig. 6) and to continued cycling at different current rates (see Supplementary Fig. 7). The outstanding rate performance has made it possible to test CuFe-TBA through 0.73 million cycles at 500 C, over which it retains 60% of its original capacity (Fig. 2b and Supplementary Fig. 7). Despite the nanosized morphology of CuFe-TBA, such high rate performance has never been reported on any PBA compound with metal cations as charge carriers. To further examine the rate behaviour of CuFe-TBA, cyclic voltammetry curves were recorded at different scan rates, revealing four pairs of redox peaks (Fig. 2c). We attribute the O1/R1 pair at low potentials to Cu⁴/Cu³ and the remaining peaks at higher potentials to Fe⁰/Fe³²,₃₅. This contrasts with the two-redox-pair behaviour of topochemistry of Na⁺, K⁺ and NH₄⁺ in CuFe-TBA (Supplementary Fig. 8). The results indicate that proton (de)insertion can reveal different chemical environments in CuFe-TBA, particularly the various hydration conditions through hydrogen bonding. Another distinction between (de)protonation and (de)insertion of Na⁺, K⁺ or NH₄⁺ within CuFe-TBA is the gap between the peak potentials (E⁺ and E⁻) of corresponding anodic and cathodic currents, as shown in Fig. 2c and Supplementary Fig. 8-10. The peak potentials are nearly identical for the pairs R2/O2, R3/O3 and R4/O4.

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Fig. 1 | Transfer of charges and energy, and three classes of PBAs. a. A schematic of the Grotthuss mechanism, in which proton conduction is operated by rearranging bonds along a water chain. b. A schematic of Newton’s cradle. c-e. Schematic structures of Berlin green, M[Fe(CN)]₆[2H₂O (c), IPB, M[Fe(CN)]₆[3.5H₂O (d) and Turnbull’s blue, M[Fe(CN)]₆[4H₂O (e)).
pertaining to proton storage in CuFe-TBA; however, the gaps of peak potentials within each pair are large for the three metal ions. The aligned cyclic voltammetry peaks are known as characteristics of thin-layer cells or redox reactions of chemisorbed species, where mass diffusion can be neglected.

The peak current, $I$, in a cyclic voltammetry curve can be related to the scan rate, $v$, by the equation $I = av^b$, where $a$ is a coefficient, and in the limiting cases where the kinetics is diffusion controlled or perfectly non-diffusion controlled (capacitive) the exponent $b$ would be either 0.5 or 1.0, respectively\(^{11,12}\). The $b$ values for the R4, R3 and R2 peaks are close to unity, indicating strong capacitive behaviour (Fig. 2d). To better demonstrate the advantages in kinetics of the proton (de)insertion inside CuFe-TBA, we also focus on the Fe$^{II}$/Fe$^{III}$ couple in evaluating the rate capability of CuFe-TBA, we also focus on the Fe$^{II}$/Fe$^{III}$ couple in evaluating the rate capability of CuFe-TBA by adopting a narrower potential range from 0.55 to 1.3 V. At an extremely high current rate of 390 A g$^{-1}$ (6,000 C or 521 mA cm$^{-2}$, where 1 C is defined as 65 mA g$^{-1}$ here), a high capacity utilization of 70% is still attainable (Supplementary Fig. 11). The fast kinetics of redox reactions would not be viable without fast proton conduction within CuFe-TBA. Measurements to verify this found proton conductivity of 3.65 × 10$^{-4}$ S cm$^{-1}$ at 298 K and 100% humidity give an activation energy ($E_a$) of 0.28 eV (Supplementary Fig. 12), where an $E_a$ value below 0.4 eV typically suggests Grotthuss conduction\(^{13,14}\).

To verify the correlation between the excellent electrochemical performance of CuFe-TBA in the H$_2$SO$_4$ electrolyte and the Grotthuss proton conduction mechanism, we used two different approaches to test the rate performance of the material under conditions where Grotthuss topochemistry is non-viable. Grotthuss conduction cannot be active in CuFe-TBA when metal ions are the inserted charge carriers\(^{15-25}\), and indeed, when storing Na$^+$, K$^+$ or NH$_4^+$ ions, CuFe-TBA delivers poorer rate performance, with $b$ exponents well below unity (Fig. 2e, Supplementary Figs. 13 and 14). A second approach to evaluate Grotthuss conduction is to interrupt the hydrogen-bonding network inside the PBA electrode to remove contiguous pathways for Grotthuss displacement\(^{26}\). IPB and BG have the same framework architecture as CuFe-TBA, but fewer anion vacancies per formula unit and thus poor connectivity of hydrogen bonding between the zeolitic cages. Stochastic models of the vacancy arrangement in IPB (discussed in ‘Characterization and simulation of the CuFe-TBA structure’) suggest that more than 80% of the hydrogen-bonding network is contiguous. As expected, both BG and IPB exhibit inferior proton (de)insertion kinetics compared with CuFe-TBA in the same acidic aqueous electrolyte (Fig. 2f and Supplementary Fig. 15). These comparative studies highlight the correlation between the Grotthuss mechanism and high rate capability of proton storage in CuFe-TBA.

Characterization and simulation of the CuFe-TBA structure

To understand the structure of the hydrogen-bonding network on which Grotthuss conduction depends, a set of advanced structural characterization experiments was performed in conjunction with density functional theory (DFT) calculations to determine the atomic structure of CuFe-TBA that hosts lattice water. Synchrotron X-ray diffraction (XRD) reveals a typical face-centred cubic structure of the CuFe-TBA framework with a space group of Fm3-m and a lattice parameter $a$ of 10.12501 Å ($R_p = 4.81\%$, $\chi^2 = 5.45$, $R_{wp}$ and $\chi^2$ reveal the quality of the fitting) (Fig. 3a). Refinement of neutron diffraction patterns from the deuterated samples reveals the presence of three distinguishable water positions of ligand water (O1), centre zeolitic water (O2) and off-centre zeolitic water (O3), respectively (Fig. 3b and Supplementary Fig. 16). Figure 3c depicts the electron density map of a unit cell, where the electron distribution of atoms can be clearly shown. Supplementary Table 2 lists the refined atomic positions and occupancies of CuFe-TBA.

To resolve the water network, DFT calculations were employed to identify the energetically favourable configuration for collections of water molecules confined in the pipework of spaces created by neighbouring ferricyanide vacancies. Calculations were performed...
using a $3 \times 1 \times 1$ supercell of the face-centred cubic lattice, which is the smallest volume that possesses the CuFe-TBA 3:2:12 stoichiometry of CuFeH$_2$O (Supplementary Fig. 17). As shown in Fig. 3d,e and Supplementary Fig. 18, after relaxation, both ligand and zeolitic water molecules cooperatively form a hydrogen-bonding network. Moreover, when CuFe-TBA is soaked in the electrolyte, it will absorb additional water into its zeolitic cages, and thus contain more lattice water than the dry samples characterized by diffraction. Therefore, the hydrogen-bonding network can only be more populous and denser than the simulated network. The DFT calculations show the connectivity of the water network within the pipe formed by two adjacent vacancies, but long-range transport also requires the vacancies to be arranged so that the pipework is percolating. Figure 3f and Supplementary Fig. 19 show the stochastic models of the vacancy pipework in $6 \times 6 \times 6$ supercells of IPB and TBA. Whereas in IPB there are 25 pipe sets and more than 80% of the pipework is percolating, in the TBA the pipework is considerably less tortuous, with just two percolating pipe systems accounting for more than 95% of the porosity. Taken together, the characterization and simulation results clearly support the
correlation between the Grotthuss mechanism and the high rate capability of CuFe-TBA.

Proton-binding sites and conduction activation energy

The protons inserted in CuFe-TBA will bind with lattice water molecules to form hydronium—H₃O⁺ (refs. 24–27). Therefore, it is critical to understand whether zeolitic or ligand water is the more favourable binding site. We employed the DFT calculations to compare the energetics of proton binding on the two sites. To save computation expense, we selected the IPB structure as the model, as it is the smallest unit cell that hosts two types of lattice water. We simulated several possible water orientations in the neutral IPB structure and chose the geometry with the lowest energy as the starting compound, as shown in Fig. 4a and Supplementary Fig. 20. We first modelled the protonated IPB that contains a ligand hydronium, where the inserted proton is highlighted in blue (Fig. 4b). For better visualization, the IPB framework is omitted and only the water molecules are shown. Interestingly, after relaxation, this proton migrates to a zeolitic water site, as displayed in Fig. 4c and Supplementary Fig. 21, which suggests a lower energy of the zeolitic water site for proton binding. To further verify this, we also computed a protonated IPB with a zeolitic hydronium, which, after relaxation, still retains the zeolitic hydronium configuration besides some subtle orientation adjustments (Supplementary Fig. 22). The results suggest that zeolitic water is energetically more favourable for proton binding. This can be rationalized by the fact that the oxygen atom of the ligand water is strongly bound to the transition metal cations, which discourages the formation of the ligand hydronium. A similar phenomenon has been reported by previous studies: a hydronium cation prevents other cations from coordinating with its oxygen (refs. 24,25).

On the other hand, the relaxation calculations support the concept of Grotthuss conduction of protons inside the CuFe-TBA structure. As shown by Supplementary Video 1, the proton ‘migrates’ along a water chain via cooperative cleavage and reconnection of the covalent and hydrogen bonds, that is, from the ligand water O₁, a starting point, to the nearby zeolitic water O₂, then to the next ligand water O₁’, and finally to zeolitic water O₂’. Such migration clearly has little to do with the vehicle mechanism. The relaxation showcases a journey of a proton driven by energetics to reach its most stable state, resembling a chemical process that works its way to the ‘equilibrium’ state. Such relaxation can, thus, simulate the local ion-electrode interaction for processes where the equilibrium state is defined by an applied potential, for example, during electrochemical potentiostatic titration tests.

To further verify our hypothesis, we calculated the energy barrier of proton hopping from a zeolitic water to the neighbouring ligand water site. As shown in Supplementary Figs. 23 and 24, the initial proton hopping and the subsequent water cluster reorientation constitute the entire activation process, where a very low energy barrier of 0.15 eV (<0.4 eV) unambiguously indicates Grotthuss conduction (refs. 23–30).

The computation results, including the percolation of the lattice water network inside CuFe-TBA, the proton migration process during relaxation and the calculated activation energy barrier, collectively suggest that the proton migration in the TBA structure is Grotthuss conduction, which rationalizes the extremely high-rate proton (de)insertion. However, we should note that the effect of fast proton conduction in electrochemical reactions can be masked by the kinetics of redox reactions as the driving force of proton conduction as well as electronic resistance of testing cells.
The Berlin green sample, $\text{Fe}^+ [\text{Fe}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ (denoted as $\text{FeFe}$-BG), was prepared by an acid-assisted precipitation method\(^3\). Typically, 80 ml of K$_2$Fe(CN)$_6$ solution (0.1 M) was added dropwise into 40 ml of 0.2 M K$_2$Fe(CN)$_6$ solution (0.10 M) under stirring. After 6 h of reaction, the dark-blue precipitate was washed with deionized water and centrifuged multiple times, and then dried in a 60° C oven overnight.

The IPB sample, $\text{Fe}_2[\text{Fe}(\text{CN})_6]_2 \cdot 3.5\text{H}_2\text{O}$ (denoted as $\text{FeFe}$-IPB), was prepared by an aqueous precipitation reaction\(^4\). Typically, 40 ml of FeCl$_3$ solution (0.15 M) was added dropwise into 40 ml of K$_2$Fe(CN)$_6$ solution (0.10 M) under stirring. After 6 h of reaction, the dark-blue precipitate was washed with deionized water and centrifuged multiple times, and then dried in a 60° C oven overnight.

**Material characterization.** The general chemical compositions of PBAs are usually expressed as A$_x$M$_m$[Fe(CN)$_6$]$_n$$\cdot$z$\cdot$H$_2$O, where A represents alkali metal\(^5\). We utilized inductively coupled plasma optical emission spectrometry (Perkin Elmer 2100DV, calibrated K, M, L calibrants) and elemental analysis (Macro Cube) to analyse C and N elements, and thermogravimetric analysis (SDTQ600, TA Instruments) to determine water content. Thus, the chemical compositions of the CuFe-TBA, FeFe-BG and FeFe-IPB were determined as Cu$_{1.44}$Fe$_{0.56}$[Fe(CN)$_6$]$_{3.46}$$\cdot$3.5$\cdot$H$_2$O, Fe$_{2.88}$[Fe(CN)$_6$]$_{2.23}$$\cdot$1.6$\cdot$H$_2$O and Fe$_{2.88}$[Fe(CN)$_6$]$_{2.23}$$\cdot$3.5$\cdot$H$_2$O, respectively. Transmission electron microscopy images of PBAs were observed on a JEOL-2010 microscope. Ex situ synchrotron XRD patterns of CuFe-TBA were collected on the 11-ID-C beamline of the Advanced Photon Source (APS), Argonne National Laboratory, where the wavelength was 0.1173 Å. XANES spectra of the Fe edge and Cu edge for CuFe-TBA samples were collected at APS on beamline 9-BM-B with an electron energy of 7 GeV and average current of 100 mA in transmission mode. The radiation was monochromatized by a Si(111) double-crystal monochromator. Harmonic rejection was accomplished with a harmonic rejection mirror. For energy calibration, the peak position of the first derivative of Co foil was adjusted to 7709 eV. XANES data reduction and analysis were processed by Athena software. For operando synchrotron XRD characterization of CuFe-TBA electrodes, a vertical focus spot size of 20 $\mu$m x 30 $\mu$m, measured as full width at half maximum. The typical exposure time was 30 s for the XRD pattern. The neutron diffraction on the deuterated CuFe-TBA was conducted at the Nanoscale Ordered Materials Diffractometer, Spallation Neutron Source, Oak Ridge National Laboratory. Samples were loaded into quartz capillaries for analysis.

**Electrochemical tests.** To prepare the working electrodes, 70 wt% PBA, 20 wt% Ketjen black carbon and 10 wt% polyvinylidene fluoride binder were first ground in a mortar to form a homogeneous slurry. The slurry was cast onto carbon fibre paper (Fuel Cells Etc, 381 μm in thickness and 1.0 mm in diameter) as the current collector\(^6\),\(^7\), and allowed to dry in an oven at 60° C. The active mass loading for PBAs is about 1.5 mg cm$^{-2}$. For higher active mass loadings of 7 and 9 mg cm$^{-2}$, we increased the mass ratio between CuFe-TBA and Ketjen black carbon to 7:2 but fixed the mass ratio of polyvinylidene fluoride binder. As a result, the mass ratio is 58.3 wt% CuFe-TBA, 16.7 wt% Ketjen black and 25.0 wt% polyvinylidene fluoride. The areal capacities of the CuFe-TBA electrodes are thus calculated as about 0.14, 0.29, 0.67 and 0.86 mAh cm$^{-2}$ for mass loadings of about 1.5, 3.0, 7.0 and 9.0 mg cm$^{-2}$, respectively. The counter electrode is a free-standing activated carbon film, which is composed of 70 wt% activated carbon, 20 wt% Ketjen black carbon, and 10 wt% polytetrafluoroethylene binder, and the mass loading of activated carbon is 30–50 mg cm$^{-2}$.

The electrochemical performance of PBAs was characterized in three-electrode Swagelok cells, in which a PBA electrode, an activated carbon film and an Ag/AgCl electrode serve as the working electrode, counter-electrode and reference electrode, respectively. The separator was Whatman filter paper, and the electrolytes were 2.0 M H$_2$SO$_4$ or 0.5 M A$_2$SO$_4$ (A = H$^+$, Na$^+$, K$^+$ and NH$_4^+$) aqueous solutions. When compared with other acid electrolytes such as CH$_3$COOH, H$_2$PO$_4$ and HCl, H$_2$SO$_4$ exhibits good ionic conductivity and a large electrochemical stability window, and was thus selected as the electrolyte for proton (de)insertion (Supplementary Fig. 26). The cell was assembled in a N$_2$-filled glovebox, and the electrolyte was purged with N$_2$ gas for 30 min before use. Note that for electrochemical tests on H$^+$-, Na$^+$ and NH$_4^+$ ions we replaced the saturated KCl solution in the reference electrode with HCl, NaCl or NH$_4$Cl solution, respectively, of the same concentration of about 4.5 M, to prevent possible contamination of the K ions from the reference electrode. After replacement of the supporting electrolyte, the reference electrodes were calibrated against the standard reference electrode accordingly. We transferred the reaction potentials from Ag/AgCl to the standard hydrogen electrode (SHE). As for operando synchrotron XRD and in situ XANES characterization, we made coin cells that contained CuFe-TBA as the working electrode and an activated carbon film as both the counter- and reference electrodes. The coin cell may transmit protons to the coin cell design was a two-electrode coin cell with a lithium metal counter electrode. The potential range for such coin cells was determined from three-electrode cells, which recorded the potential differences

**Conclusions.** In summary, we have discovered that Grothuss topochemistry leads to extremely high rate performance and extraordinarily long cycle life of CuFe-TBA as a proton battery electrode. The discovery offers a feasible approach for storage batteries based on Grothuss topochemistry in which CuFe-TBA is just one example of a plethora of hydrated solid structures that could serve as electrodes for high-power proton batteries. This study has explored to some extent the fundamental limits of high-current topolectric battery chemistry, and while the results are exciting, this is about the theoretical potential of a new technology. Tremendous challenges must still be overcome to realize ultrafast charge and discharge in practical batteries for transportation or grid energy storage. Systems operating on other charge carriers may also exhibit Grothuss-like conduction in battery electrodes, where such carriers may be OH$^-$/H$_2$O or I$^-$/I$^-$ (refs. 46,47), which warrants further investigation.

**Methods.** For the preparation of CuFe-TBA—$\text{Cu}^+ [\text{Fe}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$ (denoted as $\text{CuFe}$-TBA)—was prepared by an aqueous precipitation method\(^8\). Typically, 40 ml of Cu$_2$SO$_4$ solution (0.2 M) was added dropwise into 40 ml of K$_2$Fe(CN)$_6$ solution (0.1 M) under magnetic stirring. After 6 h of reaction, the olive-green precipitate was washed with deionized water and centrifuged multiple times, and then dried in an oven at 60° C overnight. The deuterated CuFe-TBA samples for neutron studies were prepared in a N$_2$-filled glovebox, and we used deuterated water as the reaction medium. The precipitates were rinsed with deuterated water several times and dried in a N$_2$-filled oven at 60° C overnight.
of CuFe-TBA versus the activated carbon electrode as well as versus the reference electrode. To evaluate the self-discharge, after being charged to 3.1 V versus SHE, the CuFe-TBA electrode rested at open circuit voltage for 24 h, and then discharged to 0.2 V (Supplementary Fig. 2). The robust structure and low solubility of CuFe-TBA not only give rise to an excellent cycling performance, but also rule out the possibility of the formation of toxic HCN gas in the acidic solution.

The cyclic voltammetry, GCD and rate performance of PBAs were recorded on a VMP-3 multichannel workstation (Bio-Logic Science Instruments), which has a resolution of 5 μV, an acquisition time of 20 μs and a maximum output current of 500 mA. For rate tests, the potential hysteresis in GCD is defined as the voltage gap between the charge and discharge at 50% state of charge. The cycling performance of CuFe-TBA was tested on an Arbin BT2000 system at room temperature.

**Proton conductivity tests.** The CuFe-TBA powder was first compressed into a pellet with a diameter of 10 mm and a thickness of 0.5 mm. Then the pellet was assembled into a coin cell, in which a wet cotton ball was placed to maintain the 100% humidity during tests. Electrochemical impedance spectroscopy tests were recorded on a VMP-3 multichannel workstation, where the oscillation amplitude is 20 mV and the frequencies range from 1 MHz to 0.1 Hz. The proton conductivity was determined by equation (1)\(^3\):

\[
\sigma = \frac{L}{R_{\text{S}} S}
\]

(1)

where \(\sigma\), \(L\), \(S\) and \(R_{\text{S}}\) represent the proton conductivity, thickness of pellet, contact area and bulk resistance, respectively.

We conducted electrochemical impedance spectroscopy tests at different temperatures and calculated the corresponding proton conductivities. \(E_a\) can be determined according to the following equation\(^5\):

\[
\ln(n(E)) = \ln A - E_k/k_B T
\]

(2)

where \(A\), \(E_k\) and \(E\) represents the temperature, pre-exponential factor, Boltzmann constant and activation energy for proton conduction, respectively.

**Theoretical calculations.** The Vienna ab initio Simulation Package (VASP)\(^6\) was implemented under the projector augmented wave pseudopotentials\(^7\) with the generalized gradient approximation of the Perdew–Burke–Ernzerhof\(^8\) exchange–correlation function. An energy cut-off of 550 eV with a Monkhorst–Pack\(^9\) reciprocal space grid of a 1×1×1 structure, respectively, to better show the water orientations in the relaxed structure. In order to describe the on-site Coulombic interaction, the DFT+U method\(^10\) was used, where \(U\) values were adopted from previously benchmarked literature.

To simulate the stochastic models of the vacancy pipework, we generated the 6×6×6 supercells of IPB and TBA using MATLAB (Mathworks, MATLAB R2015b). According to the chemical stoichiometry of CuFe(FN)\(_{2}\), the supercell contains 288 and 216 Fe(CN)\(_{6}\), vacancies, respectively, and these vacancies are randomly distributed in the initial state. We calculated the potential energy of these supercells in large-scale Atomic/Molecular Massively Parallel Simulator and applied the Metropolis Monte Carlo method to reorganize the distribution of vacancies\(^11\). The Metropolis Monte Carlo method is an iterative loop, where in each step a random combination of a vacancy and an anion cluster is chosen to switch positions to form a new state, and if the potential energy of the new state is lower, with a possibility of \(P = \exp(-\Delta E/k_B T)\), the loop accepts this change and starts the next step; if the potential energy is higher, we roll the ‘dice’ again\(^12\). After repeating the loop enough times (~30,000 steps), we scaled down the ‘sizes’ of Fe, C, and N atoms for clarity of the proton conduction through the hydrogen bond rearrangement. To calculate the energy barrier for proton conduction, we performed nudged elastic band simulations\(^13\). The minimum energy pathway through Grothuss conduction was monitored by forming at least four transition states between the donating and accepting water molecules, followed by obtaining the total energy at each step. In the NEB calculation, the energy cutoff was 750 eV to expand the electronic wavefunction, and a 1×1×1 Monkhorst–Pack k-point meshes were used.

**Data availability.** The additional data related to this study are available from the corresponding authors upon request.


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Author contributions

X.I. conceived the idea and designed the research. X.W. conducted the material preparation, electrochemical tests and data analyses with assistance from Y.Q. J.J.H. and T.W. performed Rietveld refinements of the synchrotron X-ray and neutron diffraction results. F.A.G. supervised the DFT calculations that W.S. and W.H. carried out. J.L. and T.W. supervised the synchrotron-based characterization and transmission electron microscopy measurements that L.M., T.L., X.B. and Y.Y. performed. J.N. collected the neutron diffraction data. All authors discussed the data and reviewed the final draft.

Competing interests

The authors declare no competing interests.

Additional information

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