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# **Electronic Supplementary Information**

# An Ultrafast Na-ion Battery Chemistry through Coupling Sustainable Organic Electrodes with Modulated Aqueous Electrolytes

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# **Experimental Details**

## Preparation of electrolytes, electrode materials and MXenes.

All the chemicals in this study were purchased from Sigma-Aldrich and were used as-received, unless otherwise discussed. Anhydrous NaClO<sub>4</sub> ( $\geq$ 99.0%) and acetamide ( $\geq$ 99.0%) are dissolved in water (purified on a Millipore MilliQ instrument) according to the molar ratio discussed in the main text. To prepare the organic electrolyte, anhydrous NaClO<sub>4</sub> was dissolved in the mixture of ethylene carbonate (50 vol%) and diethyl carbonate (50 vol%) to make a resultant concentration of 1 molar.

PTCDA nanoparticles (97%) were used the anode materials. A co-precipitation method was employed to prepare the Prussian blue analogue cathode. Typically, 40 mM of  $Cu(NO_3)_2$  aqueous solutions was mixed with 20 mM K<sub>3</sub>Fe(CN)<sub>6</sub> in a dropwise manner. The formed dark brown precipitates were collected by centrifugation, washed with distilled water, and then dried under vacuum at room temperature.

 $Ti_3C_2T_x$  MXene nanosheets were synthesized based on the previous etching-delamination-exfoliation method. To prepare the MXene interlayer, the synthesized suspension (~1 mg cm<sup>-3</sup>) of  $Ti_3C_2T_x$  MXene nanosheets was coated onto the separator by drop casting or spray coating. The MXene-modified separator was then dried under vacuum overnight at room temperature before utilization.

#### **Electrochemical experiments.**

The PTCDA electrode was prepared by drop-casting the slurry of 10% polyvinylidene difluoride, 50% active electrode materials, 40% conductive carbon black and *N*-methyl-2-pyrrolidone onto carbon fiber paper (Fuel Cell Store), followed by vacuum drying at 60 °C. The mass loading for PTCDA is 0.8-1.0 mg cm<sup>-2</sup>. The Prussian blue analogue cathode was prepared in a similar way.

All electrochemical experiments were performed on BioLogic VMP3. A homemade three-electrode cell (Figure S5) was used for electrochemical experiments. A free-standing activated carbon cloth and an Ag/AgCl electrode were utilized as the counter electrode and reference electrode, respectively. 800 µL of aqueous electrodes were used for each experiment. To evaluate the performance of PTCDA in the organic electrolyte, sodium metal pasted on a copper wire was designed as the reference electrode and free-standing activated carbon cloth as the counter electrode. Galvanostatic intermittent titration technique (GITT) curves of PTCDA in the hybrid and organic electrolytes were recorded using a current pulse for 5 min and subsequent relaxation of 30 min to realize the voltage equilibrium (current rate: 1C). The experimental details and parameters of other electrochemical experiments (e.g., ionic conductivity, transfer number) were discussed below.

### Materials characterization.

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer at 40 kV and 40 mA using Co-Kα radiation. Attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer (32 scans, resolution: 4 cm–1). Viscosity measurements were

recorded on an oscillatory rheometer (ARES-G2, TA Instruments) at room temperature. 1 mL of the liquid state electrolyte was transfer to a sample cup, and the sample was analyzed in a cone and cup geometry. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded on an Zeiss Merlin® FE-SEM at 5 kV and an FEI Titan CT electron microscope operated at 300 kV, respectively. X-ray photoelectron spectra (XPS) were collected with the use of a Thermo Escalab 250 spectrometer equipped with an Al-K $\alpha$  X-ray source (1486.6 eV). The binding energy of the target elements was calibrated to C 1s (284.6 eV). DSC plots were recorded on a DSC 250 (TA Instruments) at a ramping rate of 10 °C min<sup>-1</sup>. Liquid samples (8–10 mg) were added to Al Tzero pans with Al lids (TA Instruments) and then hermetically sealed by a Tzero Sample Press (TA Instruments).

## NMR experiments.

All liquid-state NMR experiments (e.g., one-dimensional spectra, relaxation time, two-dimensional 1H-1H nuclear overhauser effect spectroscopy (NOESY) spectra) were recorded on a Bruker 600 MHz AVANACIII NMR spectrometer equipped with BBO probe (BrukerBioSpin, Rheinstetten, Germany). Deuterated dimethylsulfoxide-D6 (99.9%, Cambridge Isotope Laboratories) was used as the field frequency lock. To avoid radiation damping effect, we designed the sample tube, as shown in Supplementary Fig. S26, to analyze the relaxation processes of hydrogen nuclei for the aqueous electrolyte (*i.e.*, *T*1 and *T*2). An inversion-recovery experiment was used to determine *T*1 values for water and amine protons, while a spin-echo technique was used to determine *T*2 values for protons. Spectral sweep width, acquisition time and other parameters were optimized to achieve  $R^2 > 99\%$  for the relaxation experiments.

## In-situ XRD experiments.

All *in-situ* XRD measurements were conducted on a Bruker D8 Twin diffractometer at 40 kV and 40 mA at room temperature. Since two different electrolytes were used to illustrate the reaction mechanism of PTCDA, we designed and developed two in-situ XRD electrochemical cells (Supplementary Fig. S8). When operating in the organic electrolyte, a beryllium window was directly used as the current collector for PTCDA (working electrode), whereas a sodium metal foil was used as the counter and reference electrode. The electrochemical cell was assembled in a MBRAUN glovebox ( $H_2O < 0.1$  ppm and  $O_2 < 0.1$  ppm). For the hybrid electrolyte, a three-electrode homemade cell was used. Importantly, a thin Parafilm tape was covered on the PTCDA working electrode to facilitate X-ray diffraction and create a gas-tight condition, in which a free-standing activate carbon cloth and an Ag/AgCl were used as the counter electrode and reference electrode, respectively. The diffraction data were collected from 5° to 30° with a collection time of 15 min for each diffraction pattern.

# Structural fittings of XRD patterns.

The in-situ data were collected on the Bruker D8 Twin diffractor. We extracted a series of data at the different charge or discharge states of the PTCDA electrode. First, Topas V6 was employed to do a le bail fitting, aiming at obtaining the refined unit cell. Then we built the structure models with the refined unit cell in Material Studio. The space group remained  $P2_1/c$ . The PTCDA unit was kept rigid in the structure unit except for slight orientation and rotation along the b and c directions due to the Na<sup>+</sup> insertion. We concluded that there were specific positions that could accommodate and locate the intercalated Na<sup>+</sup>, i.e., two oxygen species from O=C–O in PTCDA. The distance between two oxygen species from two nearby PTCDA units was around 4.2 Å. For example, two types of Na<sup>+</sup> ions with an occupancy of 0.25 and 0.05 were located between the two oxygen species from two different PTCDA units for the electrode when recharging to 2.3 V.

#### Molecular dynamics simulations.

*Ab-initio* molecular dynamics (AIMD) simulations were used in this study to illustrate the chemical environment of different electrolytes. AIMD were conducted using CP2K 9.1 package. The electrolyte structures were built based on thee organic electrolyte (NaClO<sub>4</sub> dissolved in ethylene carbonate and diethyl carbonate), the aqueous electrolyte (NaClO<sub>4</sub> dissolved in water) and two hybrid electrolytes with two different compositions ( $n_{NaClO4}$ : $n_{acetamide}$ : $n_{H2O} = 1:4:0$  and 1:4:4). The original structures of simulated electrolytes and the simulation cells with the dimension of  $10 \times 10 \times 10$  Å<sup>3</sup> were created based on Packing Optimization for Molecular Dynamics Simulations (Packmol) program. All the simulations were performed using functional PBE-GD3BJ with DZVP-MOLOPT-SR-GTH basis set, and the plane-wave basis set cutoffs of the wave functions were set at 400 eV. A time step of 0.5 fs using an isothermal–isobaric (NPT) ensemble at ambient conditions was employed for 50 ps. The barostat is set as isotropic cell with a time constant of 1000 fs. Another 40 ps production run was performed to ensure all the initial structures were fully relaxed. Snapshots of the cell geometries were sampled for five configurations at an interval of 1 ps to ensure uncorrelated samples, guaranteeing sufficient statistics to analyze the electrolyte solvation structures like radial distribution function.

# **Supplementary Figures**



**Fig. S1** FT-IR spectra of different electrolytes with (a)  $H_2O$  and (b)  $D_2O$ . In the electrolytes made with  $H_2O$ , the typical changes in the range of 2800–3800 cm<sup>-1</sup>, typically assigned to –OH stretching of water, can be observed in the hybrid electrolytes with different molar ratio of  $n_{NaCIO4}$ : $n_{acetamide}$ : $n_{water}$  (i.e., 1:4:0, 1:4:2). However, the overlapping of typical –NH<sub>2</sub> bands of acetamide and –OH bands of water, in 2800–3800 cm<sup>-1</sup> and at around 1640 cm<sup>-1</sup>, makes it challenging to distinguish how the chemical environment of the hybrid electrolytes change with the electrolyte compositions. To better illustrate the chemical environment, we prepared a series of hybrid electrolytes using deuterium oxide (D<sub>2</sub>O) (Figure S1b). Compared to the pure H<sub>2</sub>O solvent, this technique could introduce a new peak in 2050–2750 cm<sup>-1</sup> that can be attributed to the D–O stretching vibration, while the –NH<sub>2</sub> bands of acetamide appear at above 2800 cm<sup>-1</sup>. Upon introducing acetamide, the asymmetry and signal positions of the D–O stretching vibrations can be observed. More importantly, significant blue shift of the –NH<sub>2</sub> bands in acetamide can be detected, further indicating the critical role of acetamide in modulating the solvation and chemical environment of the hybrid electrolytes (e.g., disrupting the hydrogen bonding networks between water molecules).



**Fig. S2** Differential scanning calorimetry (DSC) plots of the hybrid electrolytes at different molar ratios of  $n_{\text{NaCIO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{water}}$ . When water content in the hybrid electrolytes is low, an exothermic peak corresponds to the crystallization temperature, which should be related to the presence of abundant free acetamide clusters. Upon increasing the molar ratio of water in the hybrid electrolytes, no typical crystallization or melting feature of liquid electrolytes can be seen. This is similar to the feature of hydrated electrolytes.<sup>[1,2]</sup> This is a strong indication that acetamide molecules can efficiently penetrate into hydrogen bonding networks of water molecules, which can significantly suppress the formation of water or acetamide clusters.



Fig. S3 Optical photos of the hybrid electrolytes at different molar ratios of  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}}$ . The transparent and colorless feature indicate the efficiency of our strategy in designing aqueous electrolytes.



**Fig. S4** Physical property summary of the hybrid electrolytes at different  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}}$ . Both viscosity and ionic conductivity decrease on decreasing the water content in the hybrid electrolytes. The hybrid electrolyte with  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:4$  shows well-balanced properties of low water content, high ionic conductivity, and decent viscosity and is thus chosen as the hybrid electrolyte to be studied in this work.



**Fig. S5** Photos of three-electrode homemade swagelok setup for the electrode and electrolyte performance evaluation (a), while Panel (b) shows the typical sandwich-like assembly with glassy carbon current collectors.



**Fig. S6** *Ex-situ* XPS spectra of the PTCDA electrode: (a) Na 1s and (b) O 1s core levels when working in the hybrid electrolyte with  $n_{\text{NaClO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{water}} = 1:4:4$ ; (c) O 1s core levels when operating PTCDA in the electrolyte at  $n_{\text{NaClO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{water}} = 1:4:0$  (water-free electrolyte). During discharge process in the hybrid electrolyte (Panels a and b), the storage of Na-ions at the PTCDA electrode can be observed, as evidenced by the increased intensity of Na 1s core level and the appearance of new twin peaks at lower binding energies for O 1s core level (533.6 eV  $\rightarrow$  532.8 eV for C–O and 531.5 eV  $\rightarrow$  530.7 eV for C=O). The latter indicates the carbonyl groups are the true redox-active functional group to store Na<sup>+</sup>. The absence of proton intercalation can revealed by two aspects: (1) the absence of typical O 1s feature assigned to –OH at 533.0 eV; and (2) the nearly the sample feature to the O 1s core level when operating PTCDA in the water-free electrolyte (Panel c). Additionally, we observed Na KLL auger appearing at 535.7 eV, further indicating the Na<sup>+</sup> storage during discharge.<sup>[3]</sup> The storage of Na<sup>+</sup> in highly reversible, as evidenced by the reversible changes in the Na 1s, Na KLL auger, and O 1s core levels upon recharging.



**Fig. S7** Electrochemical stability window of different electrolytes (scan rate: 10 mV s<sup>-1</sup>). All the voltammetry plots were recorded based on our homemade three-electrode setup (Figure S5). The hybrid electrolytes with different values of  $n_{\text{NaCIO4}}$ : $n_{\text{actamide}}$ : $n_{\text{water}}$  were included for comparison. It can be found that the stability window of the hybrid electrolytes can be extended when decreasing the molar ratio of water. The concentration of the aqueous NaClO<sub>4</sub> electrolyte is 3.24m. Since different electrolytes show apparently different ionic conductivities, IR compensation was conducted for all voltammetry profiles for accurate comparison.



**Fig. S8** Schematic illustrations of in-situ XRD setups for different electrolytes: (a) organic electrolytes and (b) hybrid electrolytes. Beryllium window can be used as the current collector for PTCDA directly in organic electrolytes. However, beryllium can not be used in water-containing electrolytes because of serious corrosion issue. For the hybrid electrolyte, we designed a three-electrode battery setup (Figure S8b). After a lengthy screening process, we chose parafilm to cover the PTCDA electrode to create a gas tight environment (avoiding PTCDA oxidation or reduction during operation) and allow decent X-ray diffraction signal to noise. A porous current collector was used to load PTCDA to ensure sufficient electrolyte infiltration.



**Fig. S9** *Ex-situ* SEM images of the PTCDA electrode in the hybrid electrolyte upon charging  $(n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water.}} = 1:4:4)$ , showing the interesting morphological evolution upon desodiation.



Fig. S10 *Ex-situ* SEM images of the PTCDA electrode operated in the organic electrolyte, showing insignificant morphological changes upon (de)sodiation.



**Fig. S11** Fitted crystalline structures of the PTCDA electrodes at different charge and discharge states when working in the organic electrolyte.



Fig. S12 Fitted crystalline structures of the PTCDA electrodes at different charge states (Na<sup>+</sup> deintercalation) when working in the hybrid electrolyte with  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:4$ .



**Fig. S13** Electrochemical setup to test the equilibrium potential shift in different electrolytes (the Na<sup>+</sup> intercalation reaction as a function of the Na<sup>+</sup> molality in the electrolyte). The potential of Na<sub>3-x</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> ( $x \sim 2$ ) was measured *versus* Ag/AgCl in the cell configuration shown in Panel (a). Panel (b) demonstrates the typical galvanostatic charge-discharge curves of the Na<sub>3-x</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (current rate: 0.05 A g<sup>-1</sup>), the steady plateau feature of which makes it an excellent electrode to measure the equilibrium potential shift.



**Fig. S14** Activity coefficient calculations for the hybrid electrolyte ( $n_{\text{NaCIO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:4$ ) and aqueous NaClO<sub>4</sub> electrolyte. The calculation was based on the Nernst equation. It should be noted that compared to that of the aqueous NaClO<sub>4</sub> electrolyte, the hybrid electrolyte shows increased activity coefficients, indicating the changes in solvation structures of Na<sup>+</sup> to modulate the thermodynamic properties. The activity coefficient of Na<sup>+</sup> in the hybrid electrolyte is about 20 times higher than that of aqueous NaClO<sub>4</sub> electrolytes, suggesting the unique role of acetamide in modifying the solvation structure of Na<sup>+</sup>.



**Fig. S15** Liquid-state NMR spectra of the designed in electrolytes: (a) <sup>23</sup>Na, (b) <sup>17</sup>O (H<sub>2</sub>O), (c) <sup>1</sup>H (H<sub>2</sub>O) and (d) <sup>17</sup>O (ClO<sub>4</sub><sup>-</sup>). Compared to <sup>23</sup>Na spectrum of aqueous NaClO<sub>4</sub> reference, the <sup>23</sup>Na spectra for the hybrid electrolytes show pronounced upfield shift. Additionally, the <sup>17</sup>O (H<sub>2</sub>O) resonance signals show slight upfield shift along with the broadening effect of the resonance signals when decreasing the ratio of water in the hybrid electrolyte. These results reflect that the solvation structures of Na<sup>+</sup> strongly interpenetrate in the hybrid electrolytes, while acetamide molecules play a more important role than that of water, as also confirmed by FT-IR spectra and the following molecular dynamics simulations. Remarkably, the <sup>17</sup>O (ClO<sub>4</sub><sup>-</sup>) signal is insignificantly changed upon changing the compositions of the hybrid electrolytes. This is also a strong indication that acetamide would replace water molecules in the solvation shells of Na<sup>+</sup> upon decreasing the molar ratio of water.



**Fig. S16** Liquid state <sup>23</sup>Na NMR spectra of three different electrolytes: 1m NaClO<sub>4</sub> (aq.), 3.24m NaClO<sub>4</sub> (aq.) and the hybrid electrolyte at  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:4$ . The rationale for choosing 3.24m NaClO<sub>4</sub> (aq.) as one of the control electrolytes is because it has the same molality of NaClO<sub>4</sub> to that of the hybrid electrolyte featuring  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:4$ . Taking 1m NaClO<sub>4</sub> (aq.) as the reference, the hybrid electrolyte shows more pronounced upshield and line-width broadening in comparison with that of 3.24m NaClO<sub>4</sub> (aq.). This reveals the strong shielding effect of acetamide and its role in modulating the solvation sheath of Na<sup>+</sup>.



**Fig. S17** <sup>1</sup>H NMR spectrum of acetamide, which was simulated by ChemDraw. For the pure acetamide, the amide protons show one resonance signal around 7 ppm.



**Fig. S18** Molecular dynamics (MD) simulation results of organic electrolyte and the control electrolyte with  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:0$  (water-free electrolyte). In good agreement with our spectroscopic characterizations of the electrolytes, MD simulations reveal that both the organic and control electrolytes feature contact ionic pairs, which require high energy barriers for desolvation. Considering the low ionic conductivity and high viscosity for both electrolytes, it is reasonable and rational to see the uncompetitive rate performance compared to the case when operating PTCDA in the hybrid electrolyte at  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:0$  (water-enriched electrolyte).



**Fig. S19** Galvanostatic charge-discharge plots of the PTCDA in the 3.24m NaClO<sub>4</sub> (aq.) (a) and cycling stability at 100C. We observed the irreversible plateau in the first discharge curve, which is similar to the situation of the hybrid electrolyte. Accordingly, through the control experiment in different electrolyte systems, we conclude the essential role of water in the structural and morphological changes of PTCDA. Furthermore, the cycling stability of PTCDA in the aqueous electrolyte is far less competitive compared that in the hybrid electrolyte (Figure 5 in the main text), suggesting the role of free water molecules in accelerating PTCDA dissolution during cycling.



**Fig. S20** Comparison of galvanostatic charge-discharge curves of PTCDA in the hybrid electrolytes with different  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}}$  (current rate: 1C). A low current density or charge/discharge rate was utilized here to avoid the influence from high viscosity and low ionic conductivity of the electrolyte at  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:0$ . The obvious changes of curve shapes upon introducing water into the electrolyte indicate the critical role of water in modulating the Na<sup>+</sup> storage mechanism at the PTCDA electrode. Especially, compared to the hybrid electrolyte with  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:4$ , nearly the same evolutions of voltages in the control electrolyte with  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:2$  (Figure S20c) indicate the critical role of water for morphological and crystalline changes.



**Fig. S21** Contact angle tests of different electrolytes on the PTCDA electrode. According to Panel (a), the PTCDA electrode is intrinsically hydrophobic. However, in the hybrid electrolytes, the PTCDA electrode starts becoming highly electrolyte-philic. Considering the high molar ratio of water and the unique solvation environment for the hybrid electrolytes, as confirmed by our spectroscopic characterizations and theoretical simulations, it is reasonable that water-enriched Helmholtz layer would be formed, which plays critical role for the morphological changes of PTCDA. This can be further reinforced by our following *ex-situ* characterizations of the separators.



**Fig. S22** Optical photos of the separators after cycling (>3000 cycles at 100C) PTCDA in the hybrid electrolyte at  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:4$ . (a) Scheme of the battery configuration, while other parts like reference electrode are omitted for simplicity. (b) The side of separator facing PTCDA. (c) The side of separator facing counter electrode or against PTCDA. The sharp difference of the two sides indicates slight dissolution of PTCDA and the capability of the hybrid electrolyte in suppressing the dissolution.



**Fig. S23** *Ex-situ* SEM images and EDS mapping of the separator that faces the PTCDA electrode (>3000 cycles at 100C) in the hybrid electrolyte at  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:4$ , showing the dissolution and nucleation of PTCDA on the separator.



**Fig. S24** *Ex-situ* SEM images and EDS mapping of the separator that faces the counter electrode (>3000 cycles at 100C) in the hybrid electrolyte at  $n_{\text{NaClO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{water}}$  = 1:4:4, showing the absence of PTCDA.



Fig. S25 Galvanostatic intermittent titration technique (GITT) plots of the PTCDA electrode in the hybrid electrolyte at  $n_{\text{NaClO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{water}}$  = 1:4:4 (a) and organic electrolyte (b) (current rate: 2C).



**Fig. S26** Comparison of rate capability of different battery chemistries with representative high-rate battery electrodes reported in the literature.<sup>[4-8]</sup> For better and clearer comparison, the current rates were presented as A  $g^{-1}$  instead of C-rate. Different batteries in both organic and inorganic electrolytes are included for comparison. The competitive rate capability of PTCDA in the hybrid electrolyte at  $n_{\text{NaClO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{water}}$  = 1:4:4 to the state-of-the-art high-rate battery chemistries (storing smaller cations than that of Na<sup>+</sup>) indicate the efficiency of our strategies in achieving new-generation aqueous Na-ion batteries based on low-cost and sustainable materials.



**Fig. S27** Scheme of our NMR tubes to measure both longitudinal and transverse relaxation times. Panel (a) shows a typical liquid-state NMR tube to collect NMR spectra using deuterated DMSO as the reference (locking magnetic field), while this NMR probe setup was turned to show remarkable radiation damping effect when testing the relaxation time. To overcome this challenge, we designed a new liquid-state NMR probe setup, as shown in Panel (b), to accurately measure the relaxation time through suppressing the signal intensity of proton (either from water or from acetamide) through decreasing the volume of the electrolyte significantly.



**Fig. S28** Illustration of radiation damping effect using different NMR probe setups: (a) the probe setup shown in Figure S27a and (b) the probe setup shown in Figure S27b. Radiation damping is an intrinsic physical phenomenon in all NMR experiments. Radiation damping for more nuclei is so weak that relaxation effects dominate it and make radiation damping negligible. However, for protons, the radiation damping effect can be serious. Radiation damping causes broadening in the NMR resonances of very strong signals (e.g., protons of water in Figure S28), resulting from the currents induced in the coil from the strong transverse magnetization. These are the fundamentals that we took to design the liquid NMR probe setup (Figure S27) in order to precisely measure the relaxation times of different electrolytes.<sup>[9]</sup> Figure S28a shows the standard <sup>1</sup>H (H<sub>2</sub>O) nutation profile using the classical probe setup (Figure S27a). We can observe obvious asymmetry and phase distortion problems, making it impossible to determine the 90° pulse based on maximum signal height with any accuracy. It is also very challenging to determine a reliable 180° based on the first minimum. However, after designing the new probe setup, the nutation plot is well behaved and we are able to read off the 90°, 180°, 270°, and 360° pulse durations.



**Fig. S29** Summary of *T*1 and *T*2 relaxation plots for different electrolytes and the corresponding fitting profiels. (a) T1 relaxation of H ( $-NH_2$  in acetamide) at ~6.8 ppm, (b) *T*1 relaxation of H ( $-NH_2$  in acetamide) at ~6.2 ppm, (c) *T*1 relaxation of H ( $H_2O$ ), (d) *T*2 relaxation of H ( $-NH_2$  in acetamide) at ~6.8 ppm, (e) *T*2 relaxation of H ( $-NH_2$  in acetamide) at ~6.8 ppm, (e) *T*2 relaxation of H ( $-NH_2$  in acetamide) at ~6.2 ppm, and (f) *T*2 relaxation of H ( $H_2O$ ).



**Fig. S30** 2D <sup>1</sup>H-<sup>1</sup>H Nuclear Overhauser Effect spectroscopy (NOESY) spectra of the control electrolyte with  $n_{\text{NaCIO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{water}} = 1:4:2$ . NOESY shows through-space interactions between molecules or within molecules, thus providing information about spatial proximity of protons. Noticeably, different protons show distinguished chemical shifts in the NMR spectra; one the other hand, both acetamide and water are polar molecules. In the 2D NOESY spectra, we found that the signals of H (-NH<sub>2</sub>) are negative between acetamide molecules, which indicates the dipole-dipole intermolecular interactions between acetamide molecules and thus the existence of free acetamide clusters in this control electrolyte when the water content is relatively low. When increasing the molar ratio of water to  $n_{\text{NaCIO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{water}} = 1:4:8$  (Figure S32), the NOESY signals turned into positive, which reveals the increased mobility of acetamide molecules, a critical factor to enable increased ionic conductivity and decreased viscosity for improved rate performance. Furthermore, we noticed that <sup>1</sup>H(H<sub>2</sub>O)-<sup>1</sup>H(-NH<sub>2</sub>) NOESY signals stay positive for the three electrolytes (Figure S30-S32) but get stronger upon increasing water molar ratio. This reveals the dipole-dipole interaction between water and acetamide within 0.5 nm in spatial distance, while the high mobility for both water and acetamide can facilitate solvent reorganization and solvation for enhanced rate performance.



**Fig. S31** 2D <sup>1</sup>H-<sup>1</sup>H Nuclear Overhauser Effect spectroscopy (NOESY) spectra of the control electrolyte with  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:4$ .



**Fig. S32** 2D <sup>1</sup>H-<sup>1</sup>H Nuclear Overhauser Effect spectroscopy (NOESY) spectra of the control electrolyte with  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:8$ .



**Fig. S33** Photos of the diffusion experiments. Liquid-phase diffusion experiments were conducted in an H cell configuration using acid blue 113 as a tracker. Acid blue 113 was employed to simulate the discharged product of PTCDA upon sodiation because of its negatively charged feature and similar structures to the discharged product of PTCDA. Acid blue 113 (5 mM) and pure water were separated by the separator with or without MXene interlayer. In the absence of MXene interlayer, the dye can diffuse rapidly through the separator. However, the crossover rate decreased sharply when introducing the negatively charged MXene interlayer. This is a strong indication of the critical role of negatively charged MXene in suppressing the dissolution of PTCDA during charge and discharge.



**Fig. S34** Characterization of the MXene interlayer. TEM image shows the nanosheet feature (Figure S33a). MXene nanosheets can be made into nice suspensions,<sup>[10]</sup> which makes it feasible to design and fabricate MXene-coated separator at scale through drop casting or spray coating. This is different from conventional filtration method to prepare MXene films. On the one hand, our drop casting or spray coating are much more time-saving and straightforward to fabricate the interlayers at scale; on the other hand, the separator can perform as a scaffold, which ensures the high mechanical stability of the interlayer.



**Fig. S35** Electrochemistry setup used to test the transfer number of our MXene interlayer. Please see details in Supplementary Note S4 for calculation details.



**Fig. S36** (a) Electrochemistry setup designed to evaluate the ionic conductivity of different interlayers and the corresponding electrochemical impedance spectroscopy (EIS) plots (b). Please see details in Supplementary Note S5 for calculation details. Herein, two additional separators were used to create a sandwich-like configuration, which is important to precisely measure ionic conductivity when including electrically MXene interlayers. Additionally, a graphene oxide (GO) interlayer was included for comparison since GO features similar surface chemistry to that of MXene. We noted that the introduction of GO interlayer can increase the resistance and decrease the ionic conductivity. This is related to the soft nature of GO nanosheets and tight stacks of GO nanosheets, which significantly impede the ionic transport across the GO interlayer. This further highlights the unique advantages of the MXene interlayer in ensuring ionic transport and prohibiting the dissolution of the PTCDA electrode.



**Fig. S37** *Ex-situ* SEM images of our MXene interlayer after cycling tests (current rate: 100C) in the hybrid electrolyte at  $n_{\text{NaClO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{water}}$  = 1:4:4. The structural integrity can be well preserved, indicating the efficiency and stability of the MXene interlayer in suppressing the dissolution issue of the organic PTCDA electrode.



**Fig. S38** Galvanostatic charge-discharge curves of the Prussian blue analogue (copper hexacyanoferrate) (a) and the corresponding cycling stability at 10C (b). The electrochemical experiments were done in the hybrid electrolyte at  $n_{\text{NaClO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{water}} = 1:4:4$ . The Prussian blue analogue was synthesized according to the previous literature. The good rate performance and cycling stability indicate the capability of the Prussian blue analogue cathode towards efficient storage of Na<sup>+</sup> in the hybrid electrolyte.



**Fig. S39** Battery performance of the full Na-ion battery with the configuration of PTCDA anode, Prussian blue analogue (PBA) cathode, MXene interlayer, separator, and hybrid electrolyte at  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}}$  = 1:4:4 (a). (b) Galvanostatic charge-discharge profiles at different rates. (c) Cycling stability test at a current rate of 20 C.

# **Supplementary Tables**

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State	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (ų)	Na site	Na occupancy
Dis. to 2.1V	3.76	19.34	10.96	90	95	90	793.96	4e	0.25
Dis. to 1.5V	3.725	19.012	10.76	90	96.24	90	757.5	4e	0.50
Rech. to 2.3V	3.725	19.012	10.76	90	96.24	90	757.5	4e	0.40
Rech. to 3.0V	3.74	19.038	10.77	90	96	90	762.65	N.A.	N.A.

**Table 1**. Crystalline structure parameters of the PTCDA electrode at different charge or discharge states when working in the organic electrolyte (NaClO<sub>4</sub> dissolved in ethylene carbonate and diethyl carbonate).

**Table 2**. Crystalline structure parameters of the PTCDA electrode at different charge or discharge states when working in the hybrid electrolyte with  $n_{\text{NaClO4}}$ : $n_{\text{acetamide}}$ : $n_{\text{H2O}}$  = 1:4:4.

State	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (ų)	Na1 site	Na1 occupancy	Na2 site	Na occupancy
Pristine	3.77	19.32	10.74	90	96.4	90	777.29	N.A.	N.A.	N.A.	N.A.
Dis. to 2.1V	3.78	19.26	10.75	90	96.08	90	778.22	4e	0.25	N.A.	N.A.
Dis. to 1.9V	3.60	21.89	12.45	90	97.7	90	972.19	4e	0.375	N.A.	N.A.
Dis. to 1.6V	3.79	19.53	10.94	90	96.2	90	805	4e	0.25	2d	0.25
Rech. to 2.1V	3.76	19.38	10.81	90	95.84	90	783.6	4e	0.25	2d	0.19
Rech. to 2.3V	3.79	19.42	10.72	90	95.94	90	784.8	4e	0.3	N.A.	N.A.
Rech. to 3.0V	3.76	19.28	10.15	90	95.64	90	733.4	N.A.	N.A.	N.A.	N.A.

# **Supplementary Note S1**

Water in the hybrid electrolyte was shown to be critical to enable the morphological change and the high rate capability. The PTCDA electrode is highly hydrophobic (Figure S21), while the PTCDA electrode is highly electrolyte-philic for the hybrid electrolytes like the one with compositions at  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}}$ = 1:4:4. This hybrid electrolyte still features high molar ratio of water. Furthermore, it is noteworthy that during the cycling performance test (Figures S22-S24), the dissolution of PTCDA can be efficiently suppressed in the hybrid electrolyte. On the other hand, the slight dissolution can be still observed, and we did not see the deposition of PTCDA on the separator on the side against the PTCDA electrode. It is reasonable to presume that it is because of the accumulation of the slightly dissolved PTCDA in the hybrid electrolyte during cycling. This is different from the serious shuttling effect (soluble polysulfur species transfer to the anode in a fast fashion) typically happening in organic lithium-sulfur batteries. Accordingly, we hypothesized that it is well-balanced properties of the hybrid electrolyte creates a unique interfacial feature like slight dissolution of PTCDA upon sodiation. This is important to initiate the morphological changes of PTCDA, similar to other heterogeneous liquid-solid electrode reaction (e.g., sulfur). Indeed, the downsizing phenomena of organic electrodes in aqueous electrolyte has also been found for other cations (e.g., Mg<sup>2+</sup>, Ca<sup>2+</sup>) storage.<sup>[11,12]</sup> To conclude, our experimental and simulation results provide a reasonable mechanism for the morphological and structural changes of organic monomer electrodes during charge/discharge.

*T*1 relaxation is the process by which the net magnetization ( $I_t$ ) grows to its initial maximum value ( $I_0$ ) parallel to  $B_0$  based on the inversion-recovery method. *T*1 is defined as the time required for the *z*-component to reach (1 – 1/*e*) or about 63% of its maximum value ( $I_0$ ). Accordingly, the following equation can be used to fit the measured data points and to acquire the value of *T*1 for specific protons (e.g.,  $-NH_2$ , -OH) of different electrolytes:

$$I_t = I_0 \left[ 1 - 2 \exp\left(-\frac{t}{T1}\right) \right]$$

wherein *t* is the time of relaxation,  $I_t$  is the magnetization at time *t*,  $I_0$  is the maximal magnetization and *T*1 is the time required to reach (1 - 1/e) of  $I_0$ .

T2 relaxation is the process by which the transverse components of magnetization  $(I_{xy})$  decay or dephase. Indeed, T2 is a time constant for the decay of transverse magnetization arising from natural interactions at the atomic or molecular levels. Accordingly,  $T_2$  is the time that is needed for the transverse magnetization to fall to ~ 37% (1/e) of its initial magnetization or maximal magnetization. The equation below is employed to calculate T2 values of specific protons in the electrolytes:

$$I_t = I_0 \exp\left(-\frac{t}{T2}\right)$$

where T2 is time needed to fall to 1/e of the maximal magnetization.

Standard rate constant can be presented as below:<sup>[13-15]</sup>

$$k_0 = A \cdot v_R^{1-\theta} \cdot T 1^{-\theta} \cdot \exp\left(-\frac{\Delta G^*}{RT}\right)$$

wherein A is the portion of the pre-exponential factor which is typically independent of the solvents.  $v_{\rm R}$  is the frequency associated with a reaction path not affected by the solvents. T1 is the longitudinal relaxation time.  $\Delta G^*$  is the Gibbs free energy of activation.  $\theta$  is a fraction between 0 and 1, which depends on the relative sizes of the inner- and outer-sphere reorganization energies.  $\Delta G^*$  is the Gibbs activation energy containing inner- and an outer-sphere reorganization energy components. "Outer-sphere" represents a reaction between two species in which the original coordination spheres are well maintained during the electron transfer process. Differently, the "inner-sphere" reaction occurs in an activate complex where the ions share one ligand. Reactions involving outer-sphere electron transfer can be treated in a more general way than the inner-sphere reaction pathway. However, in practical electrochemical redox reactions like battery electrodes especially intercalation chemistry, the more complicated inner-sphere reaction mechanism dominates. Actually, solvation sheath environment is a key factor that can influence the reorganization processes. For our hybrid electrolyte with  $n_{\text{NaClO4}}:n_{\text{acetamide}}:n_{\text{water}} = 1:4:4$ , acetamide started displacing water in the solvation shells of Na<sup>+</sup>, as confirmed by spectroscopic results and MD simulations. Considering the chemical nature similarity between both acetamide and water, the four-fold decreases in T1 can increase the rate constant by roughly four times. This is consistent with the proposed mechanism and the general framework of Marcus theory when taking the contributions of inner- and outer-sphere reorganizations into consideration for heterogeneous redox reactions.<sup>[13,16]</sup>

The capability of our MXene interlayer in conducting Na<sup>+</sup> with high selectivity can be first evaluated by the transfer number of Na<sup>+</sup>. The electrochemistry setup was shown in Figure S35. The fundamental is based on the electromotive force formed by concentration difference of two electrolytes. Relatively low-concentration electrolytes were used to ensure the application of the Debye-Hückel limiting law in calculating activity of the aqueous electrolytes. Accordingly, the following equation was used:

$$\Delta E = 2t_{-}\frac{RT}{nF}\ln\frac{a_{10mM}}{a_{2mM}}$$

wherein  $\Delta E$  is the tested potential difference (electromotive force) of two electrodes in different aqueous electrolytes.  $\Delta E$  can be measured by a potentiostat (Figure S35b). *t*<sub>-</sub>, *a*<sub>10mM</sub>, and *a*<sub>2mM</sub> are denoted as the transfer number of anions, activity of 10 mM NaClO<sub>4</sub> (aq.), and activity of 10 mM NaClO<sub>4</sub> (aq.), respectively. *R*, *T*, *n*, and *F* represent ideal gas constant, temperature, number of electrons transferred, and Faraday constant. According to the Debye-Hückel limiting law, we can have:

$$\log_{10} \gamma_{\pm} = -A \left| z_{Na^{+}} z_{ClO_{4}^{-}} \right| \frac{\sqrt{I}}{1 + \sqrt{I}}$$
$$I = \frac{1}{2} \Sigma c_{i} z_{i}^{2}$$

where A is a constant that depends on temperature (for water,  $A = 0.51 \text{ mol}^{-1/2}$  at 293 K).  $\gamma_{\pm}$  is the mean activity coefficient of the electrolyte.  $c_i$  and  $z_i$  are denoted as the concentration and charge number of ionic species *i*, respectively. I is the ionic strength of the solution. Accordingly, the activity of the electrolyte can be derived through the following equation:

$$a_{10mM} = \gamma_{\pm(10mM)} c_{10mM}$$
$$a_{2mM} = \gamma_{\pm(2mM)} c_{2mM}$$

Eventually, the transfer number of Na+ for our MXene interlayer can be calculated based on the following:

$$t_{+} = 1 - t_{-}$$

where  $t_+$  is transfer number of the cation, herein, Na<sup>+</sup>. Through measuring  $\Delta E$  and the calculation of the activity of two aqueous electrolytes,  $t_+$  is determined to be 0.884. This indicates the excellent Na<sup>+</sup> transfer properties of the MXene interlayer due to its unique structure and surface chemistries.

The ionic conductivity of the interlayer can be tested through a symmetric battery design (coil cell), as illustrated in Figure S36. The volume of the electrolyte was 100  $\mu$ L. Then, EIS spectra was recorded on Bio-Logic VMP3 in the frequency range of 0.1–200k Hz. The following formula was used to calculate ionic conductivity:

$$\sigma = \frac{L}{A \times R_b}$$

wherein  $\delta$  is the ionic conductivity, *L* is the thickness, *A* is the are, and *R*<sub>b</sub> is the resistance of the electrolyte from the high frequency intercept of the EIS spectrum on the *Z*<sub>*Re*</sub> axis. The conductivity cell constants were predetermined using 0.01M aqueous KCl standard solution at room temperature. Accordingly, after introducing the MXene interlayer, the ionic conductivity is determined to be 26.1 mS cm<sup>-1</sup>, still comparable to that of the hybrid electrolyte (28.6 mS cm<sup>-1</sup>) at *n*<sub>NaClO4</sub>:*n*<sub>acetamide</sub>:*n*<sub>water</sub> = 1:4:4. Therefore, the high transfer number and high ionic conductivity enabled by the MXene interlayer indicate its capability to ensure the battery performance.

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