Supporting Information

Proton-hopping charge storage mechanism of ionic one-dimensional coordination polymer for high-performance supercapacitors

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1. Experimental

1.1 Preparation of ZnPIm

Zinc oxide (81 mg, 1 mmol) was firstly mixed with imidazole (136 mg, 2 mmol) in presence of ethanol (500 µL) and phosphoric acid (205 µL, 3 mmol). The mixture was then put in a mortar and ground for 10 minutes. The white powder was collected by washing with ethanol and dried at 100 °C overnight.

1.2 Fabrication of symmetric supercapacitor

The electrodes were prepared by dispersing the ZnPIm active material, conductive carbon black, and PVDF binder in a weight ratio of 80:10:10 in N-Methylpyrrolidone (NMP) and then sonicated for 1 h to form a homogeneous suspension. The suspension was coated on the carbon fiber paper (CFP) substrate (diameter of 1.58 cm) by a spray-coating technique under a pressure of 30 psi and dried at 60 °C overnight. The amount of active material on each electrode is about 1.2-1.5 mg. The hydrolyzed polyethylene (PE) film with a thickness of 25 µm used as a separator was soaked in 1 M H_2SO_4 for 20 min and inserted between the electrodes. The symmetric supercapacitor cells were assembled in CR2016 coin-cells via a hydraulic press at 800 psi for 5s.

Galvanostatic charge-discharge (GCD) was tested using the NEWARE battery test system in the voltage range between 0 to 1.6 V at applied specific current of 1 to 5 A g^{-1}. Cyclic voltammetry (CV) was carried out using the Metrohm AUTOLAB potentiostat (PGSTAT 302N) between 0 to 1.6 V at 10-100 mV s^{-1}. Electrochemical impedance spectra (EIS) was conducted with an applied amplitude of 0.01 V at the frequency range of 0.01 Hz - 10 kHz on the Metrohm AUTOLAB potentiostat (PGSTAT 302N).

2. Electrochemical calculation

The cell specific capacitance (C_{cell}) can be calculated from CV and GCD by the following equations (S1) and (S2), respectively;

$$C_{cell,\ CV} = \frac{Q}{\Delta V_{CV}\ x\ m} \tag{S1}$$

$$C_{cell,\ GCD} = \frac{I\ x\ \Delta t}{\Delta V_{GCD}\ x\ m} \tag{S2}$$

The specific capacitance (C_s) based on a single electrode can be calculated by the following equation (S3);

$$C_s = 4C_{cell} \tag{S3}$$

where Q is an average charge in the discharge process of CV curve (Coulomb), ΔV_{CV} is the cell voltage window in the discharge process of CV curve (V), I is the applied current (A), ΔV_{GCD} is the cell voltage of discharge process excluding the iR drop (V), Δt is the discharge time, and m is the total mass of active materials on both positive and negative electrodes.

The relaxation time (τ_0) can be calculated from the active power (|P|), reactive power (|Q|), and complex power (|S|) by the following equation (S4-S11);

$$P(\omega) = \omega C''(\omega)\left|\Delta V_{rms}\right|^2 \tag{S4}$$

$$Q(\omega) = -\omega C'(\omega)\left|\Delta V_{rms}\right|^2 \tag{S5}$$

$$S(\omega) = P(\omega) + jQ(\omega) \tag{S6}$$

$$C^{'}(\omega) = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2} \tag{S7}$$

$$C^{'}{'}(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2} \tag{S8}$$

$$\left|\Delta V_{rms}\right|^2 = \Delta V_{max}/\sqrt{2} \tag{S9}$$

$$\omega = 2\pi f \tag{S10}$$

$$\tau_0 = 1/2\pi f_0 \tag{S11}$$

where C'(ω) is the real part of the complex capacitance, C''(ω) is the imaginary part of the complex capacitance, V_{max} is the maximum amplitude of the applied voltage, Z'(ω) is the real part of the complex impedance, Z''(ω) is the imaginary part of the complex impedance, Z(ω) is the complex impedance, ω is the angular frequency, and f_0 is the resonance frequency.

The Energy density (E) and Power density can be calculated by the following equation (S12-S13);

$$E = \frac{1}{2} x\, C_{cell}\, x\, \Delta V^2 \tag{S12}$$

$$P = \frac{V_0^2}{4R_{cell}} \tag{S13}$$

where V_0 is the initial voltage of the device and R_{cell} is the cell's resistance from GCD.

3. Computational methods

All calculations were performed within the Vienna Ab-initio Simulation Package (VASP)[1, 2]. Projector augmented-wave (PAW) pseudopotentials were used to account for electron–ion interactions. The generalized gradient approximation (GGA)[3] with the Perdew–Burke–Ernzerfhof (PBE) functional[4] was used to treat the exchange–correlation interaction between electrons. The empirical correction according to Gimme's scheme (DFT-D2)[5] was used to describe the long-range van der Waals interactions. An on-site Hubbard term U–J[6] of 7.0 eV was also applied to Zn for treating the localization of its 3d-electrons more accurately. The value of this term (7.0 eV) was taken from ref. 7. The Brillouin zone sampling was performed at the Γ-point. The energy cutoff was set to 400 eV and the convergence thresholds for full geometry optimizations were 10^{-5} eV and 0.05 eV/Å for total energy and ionic force, respectively. The $[Zn(HPO_4)\text{-}(H_2PO_4)_2](ImH_2)_2$ unit cell used in this work was generated from its crystal structure[8]. The optimized P−OH and P=O distances were in the range of 1.58-1.60 and 1.52-1.53 Å, respectively, in good agreement with the experimental values. The energy profiles for the proton movement in $Zn(HPO_4)\text{-}(H_2PO_4)_2](ImH_2)_2$ were calculated with the nudged elastic band method (NEB).

4. XPS results

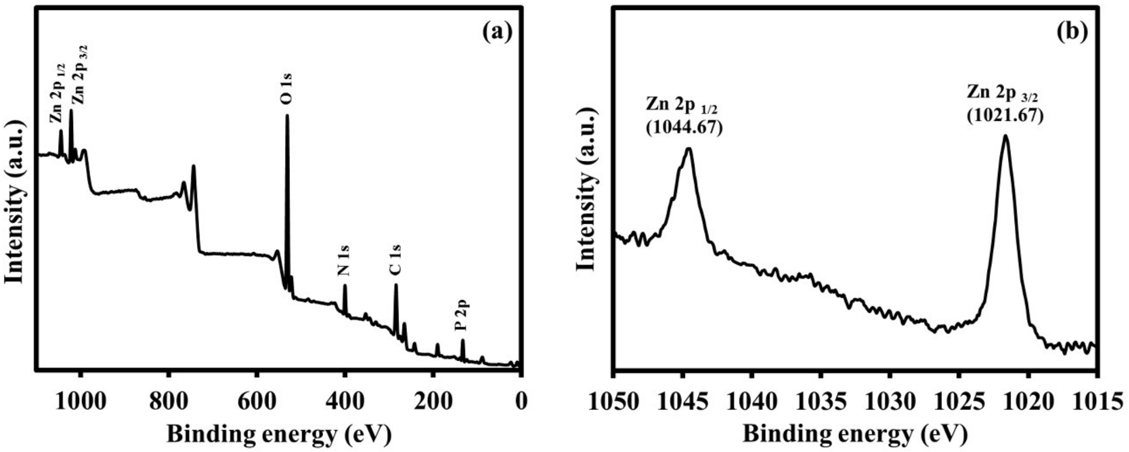

Fig S1. (a) Wide scan XPS spectrum and (b) Zn 2p narrow scan spectrum of ZnPIm.

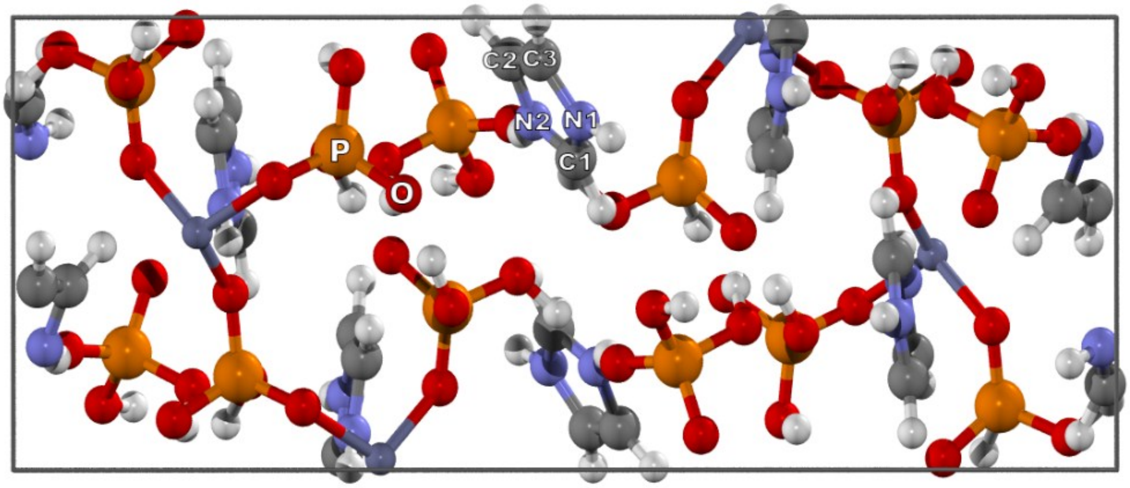

Fig S2. All possible sites for proton adsorption in the [Zn(HPO_4)-(H_2PO_4)$_2$](ImH_2)$_2$ framework.

Table S1. The relative energy of proton adsorption on different sites in the [Zn(HPO_4)-(H_2PO_4)$_2$](ImH_2)$_2$ framework.

Adsorption positions	**Relative energy (eV)**
P=O	0.00
C1	0.21
C2	1.94
C3	1.35
N1	0.89
N2	0.80

References

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