

## Supporting Information

### **Electrolyte regulation enhances the stability of Prussian blue analogues in aqueous Na-ion storage**

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### Calculation of Na<sup>+</sup> ion diffusivity

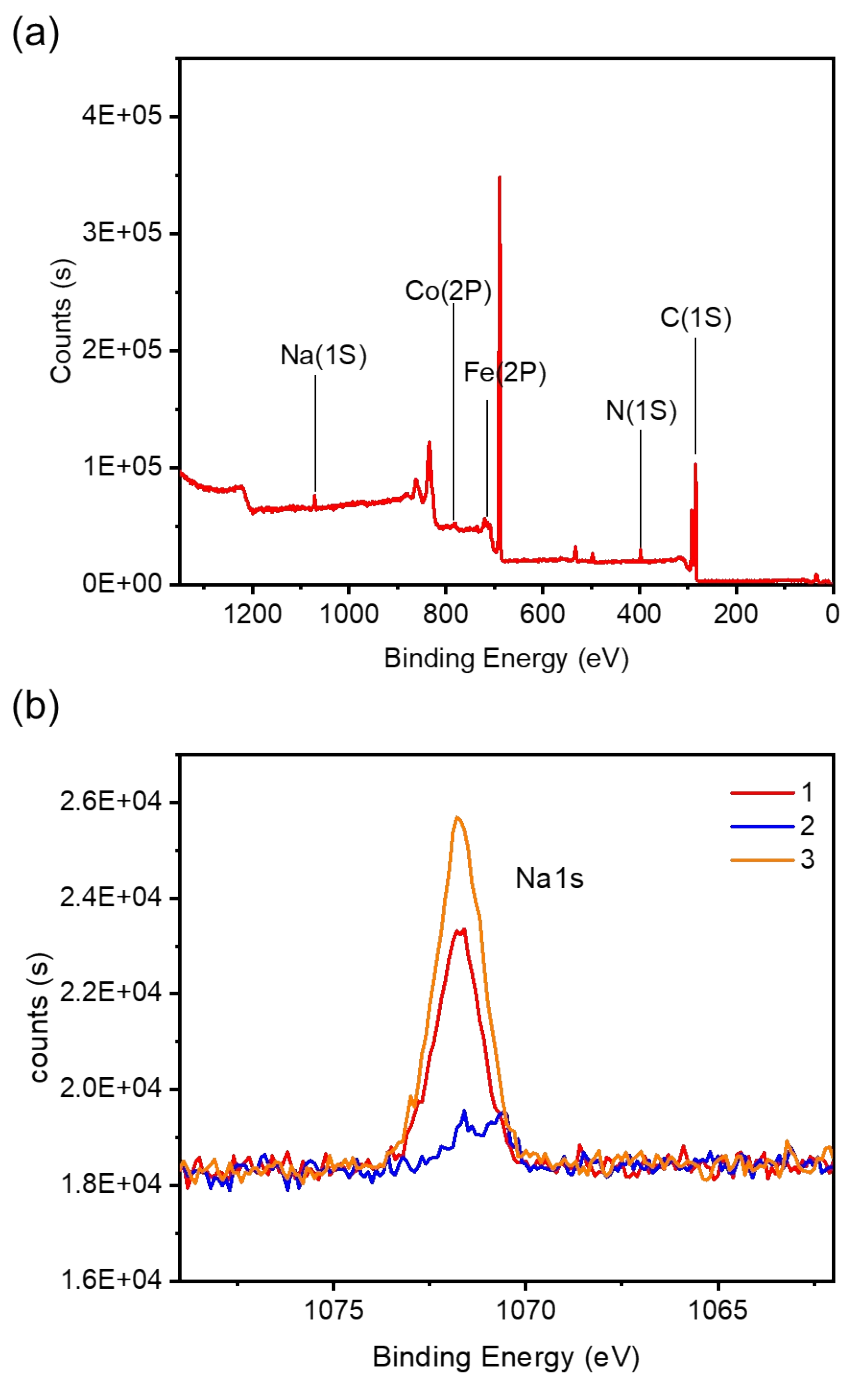
The Na<sup>+</sup> ion diffusivity of CoHCF has been calculated based on the result of electrochemical impedance spectroscopy (EIS) (Figure 2d), the equivalent electric circuit is shown in the insets, in which  $R_{SEI}$  and  $R_{CT}$  severally represent the solid electrolyte interface resistance and charge-transfer resistance, and  $Z_W$  represents the Warburg impedance. The Na<sup>+</sup> ion diffusivity of the CoHCF can be calculated with following formula given as follow,

$$D = \frac{R^2 T^2}{2 A^2 n^4 F^4 C^2 \sigma^2} \quad (3)$$

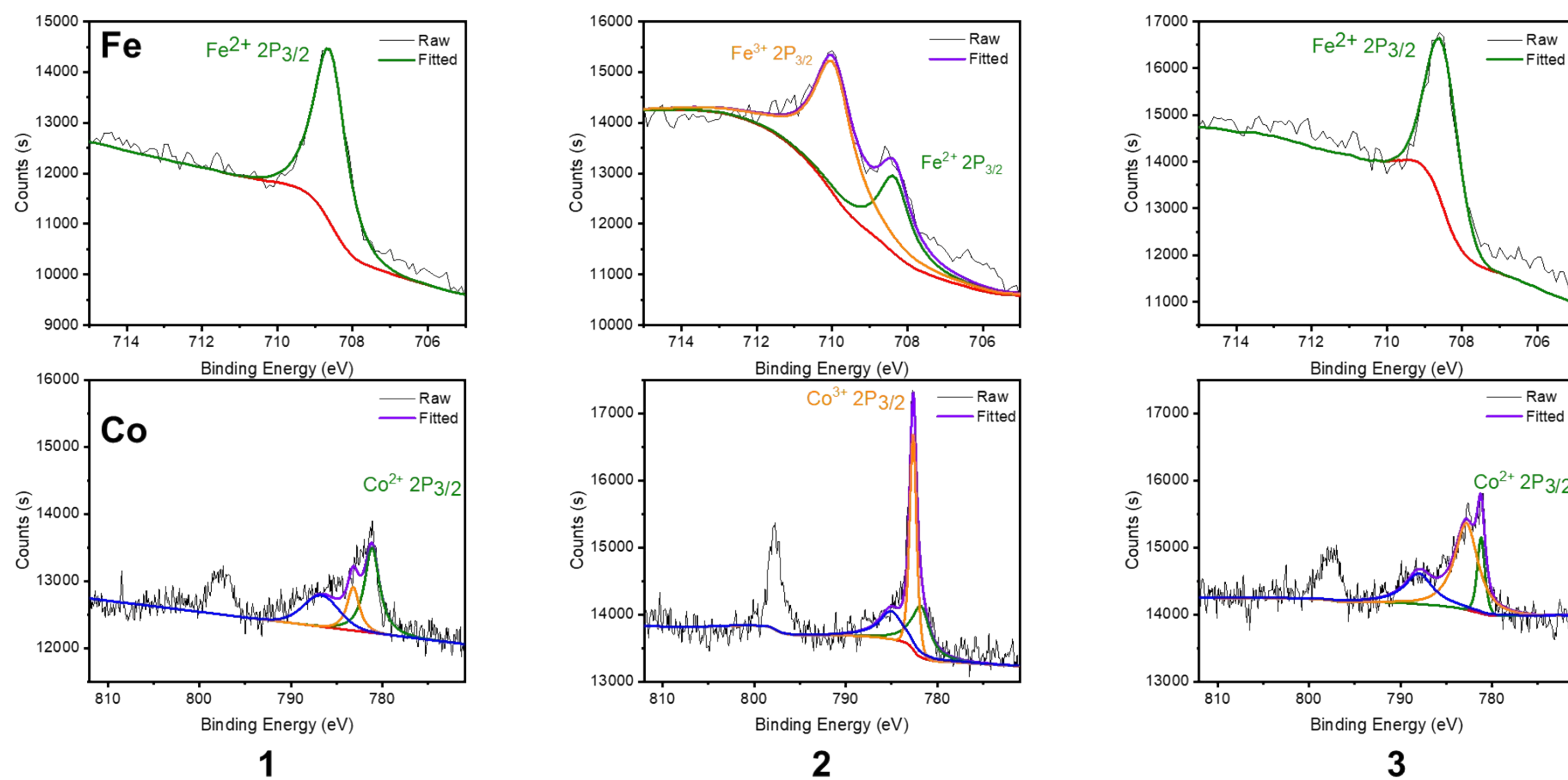
where  $R$  is gas constant (8.314 JK<sup>-1</sup> mol<sup>-1</sup>),  $T$  is the room temperature (298 K),  $A$  is the surface area of the electrode ( $3.85 \times 10^{-5}$  m<sup>2</sup>),  $n$  is the number of the electrons transferred in the electronic reaction ( $n = 2$  in this work),  $F$  is the Faraday constant (96485 C mol<sup>-1</sup>),  $C$  is the concentration of Na<sup>+</sup> in CoHCF electrode, and  $\sigma$  is the slope of the line  $Z' - \omega^{-1/2}$  (as shown in the insets of Figure 2d, the  $\sigma$  values is 40.7), Hence, the calculated  $D_{Na}$  of CoHCF is  $1.72 \times 10^{-14}$  cm<sup>2</sup> s<sup>-1</sup>.

**Table S1** Elemental contents (wt%) of as-prepared Na<sub>2</sub>CoFe(CN)<sub>6</sub> material

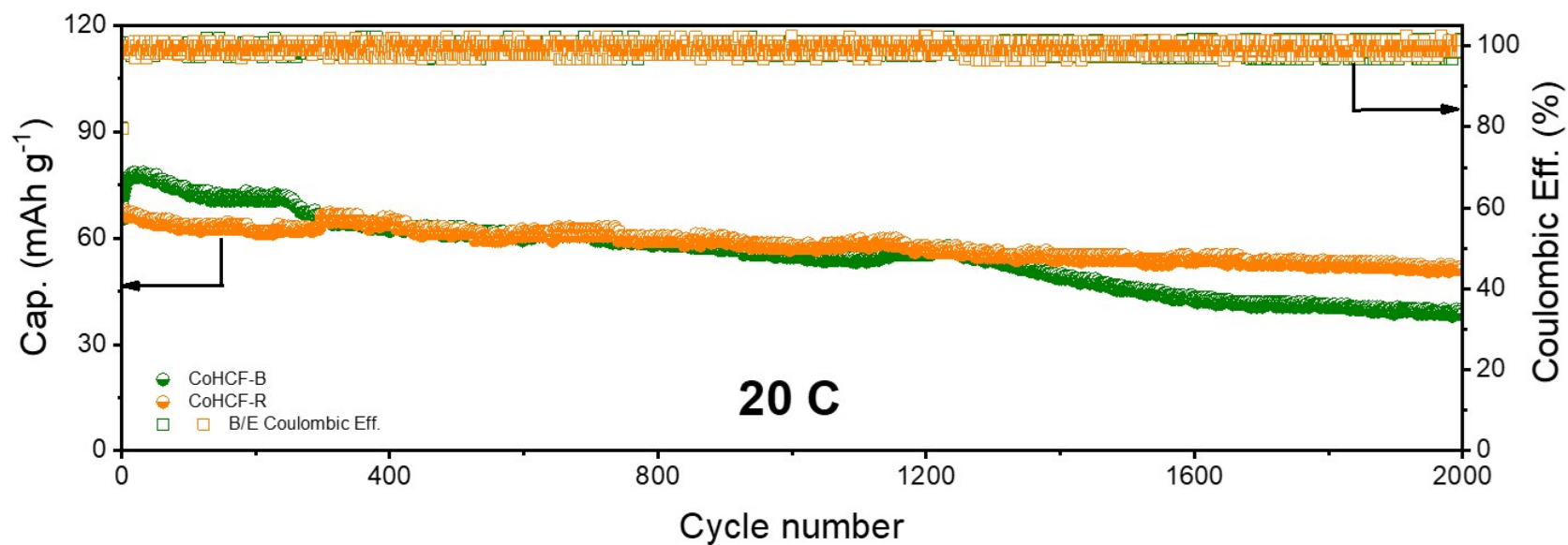
	Na	Co	Fe	C	N	H
CoHCF	10.44	17.79	14.30	19.32	22.63	1.74



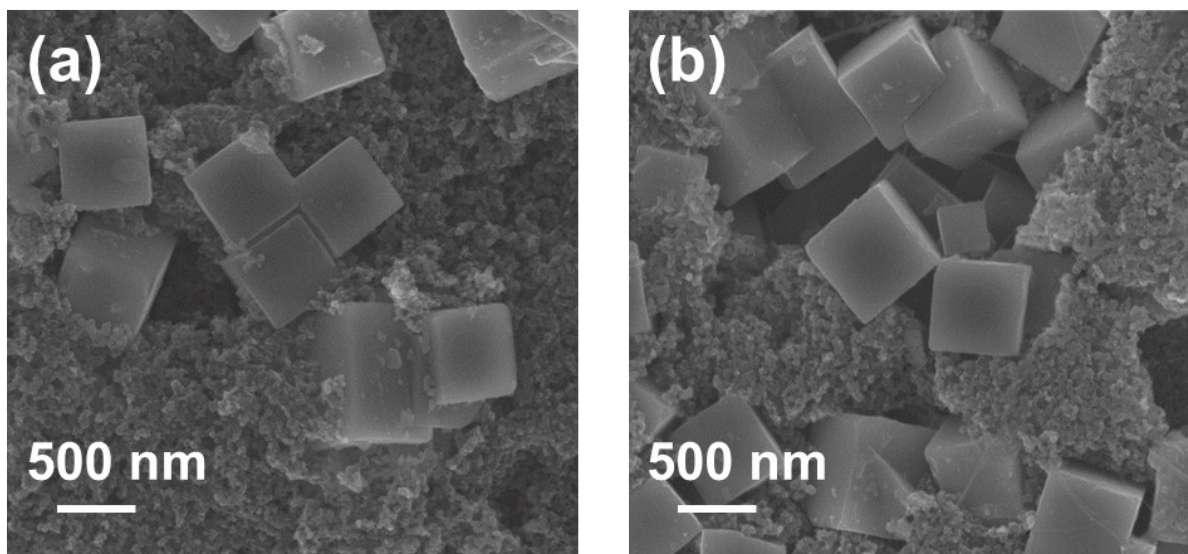
**Figure S1** XPS spectra of (a) 1 initial state, and (b) Na 1s in three states (1. initial state, 2. fully charged to 1 V, 3. fully discharged to 0 V).



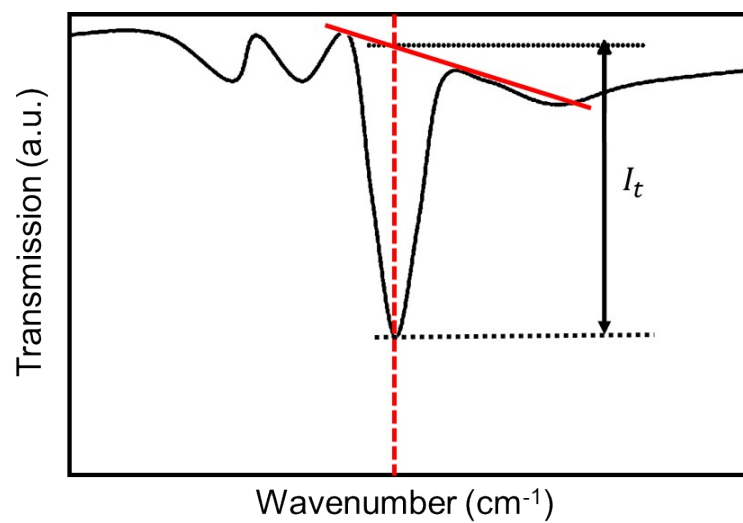
**Figure S2** XPS spectra of Fe 2p and Co 2p in three states (1. initial state, 2. fully charged to 1 V, 3. fully discharged to 0 V).



**Figure S3** Cycle performances of CoHCF-B and CoHCF-R at a current density of 20 C, 1 C=120 mA g<sup>-1</sup>.



**Figure S4** SEM images of the CoHCF-B (a) before (b) after 100cycles.



**Figure S5** The specific value of  $I_t$  to calculate the relative intensity.