Supporting Information

Engineering the modulation of active sites and pores of pristine metal-organic frameworks for high-performance sodium-ion storage

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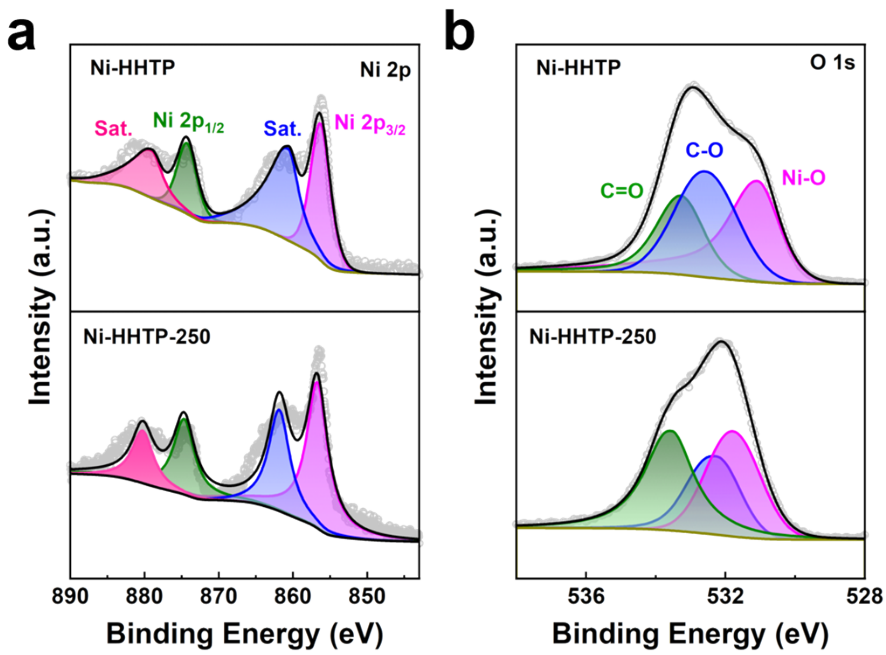

Fig. S1 High resolution XPS of (a) Ni 2p and (b) O 1s in the pristine Ni-HHTP and the Ni-HHP-250.

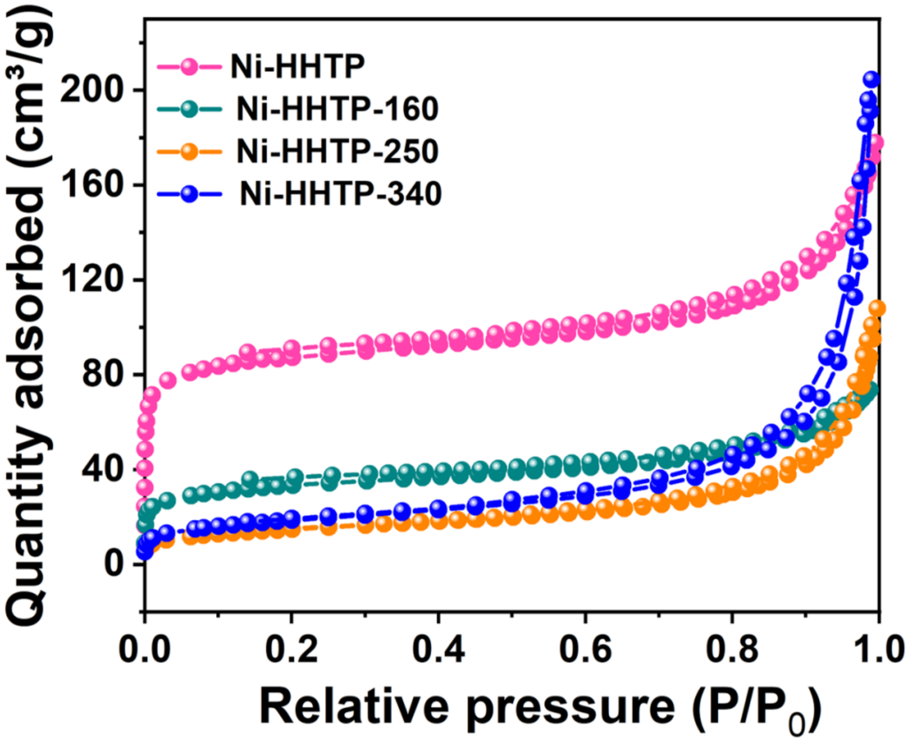

Fig. S2 Nitrogen adsorption and desorption isotherms of the pristine Ni-HHTP sample and calcined Ni-HHTP samples.

The specific surface areas of the Ni-HHTP sample, the Ni-HHTP-160 sample, the Ni-HHTP-250 sample and the Ni-HHTP-340 sample are 296.6 m^2/g, 115.9 m^2/g, 53.3 m^2/g and 66.0 m^2/g. Compared with the Ni-HHTP, specific surface areas decreased in the calcined samples. The Ni-HHTP-250 sample owned the smallest specific surface area. Although the adsorption of sodium ions was minimal, the small specific surface area reduced side reactions with the electrolyte. [1]

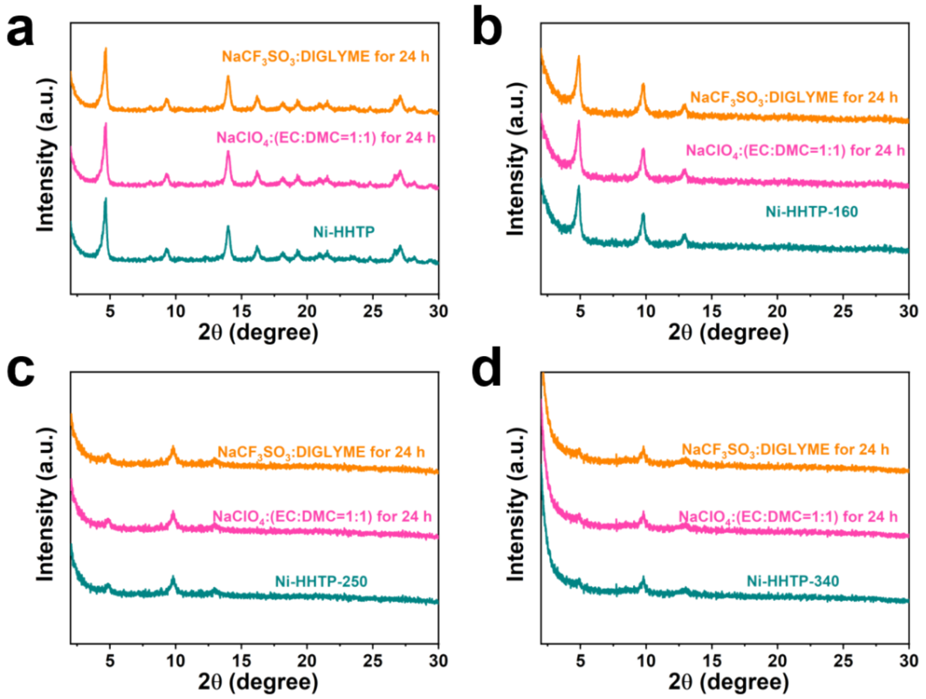

Fig. S3 The XRD patterns of the Ni-HHTP sample, the Ni-HHTP-160 sample, the Ni-HHTP-250 sample and the Ni-HHTP-340 sample after soaking in different electrolytes for 24 h.

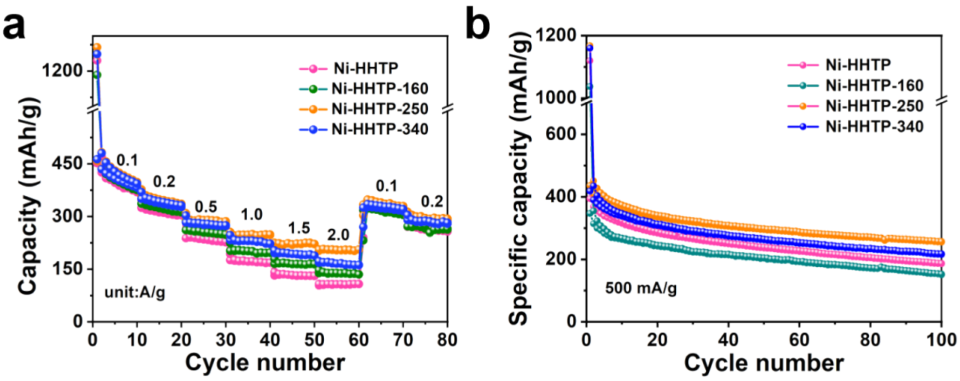

Fig. S4 (a) Rate performances of the pristine Ni-HHTP sample and calcined Ni-HHTP samples at various current rates from 100 to 2000 mA g^{-1}. (b) Cycling properties at 500 mA h g^{-1} of the Ni-HHTP-250 sample and the Ni-HHTP-340 sample.

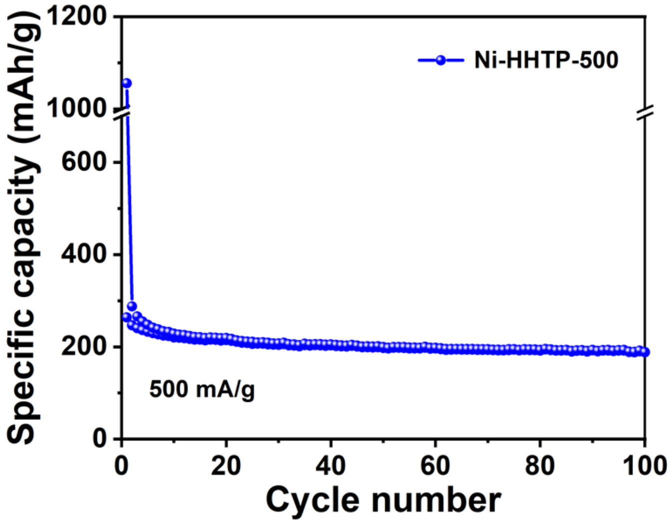

Fig. S5 Cycling property at 500 mA h g^{-1} of the Ni-HHTP-500 sample.

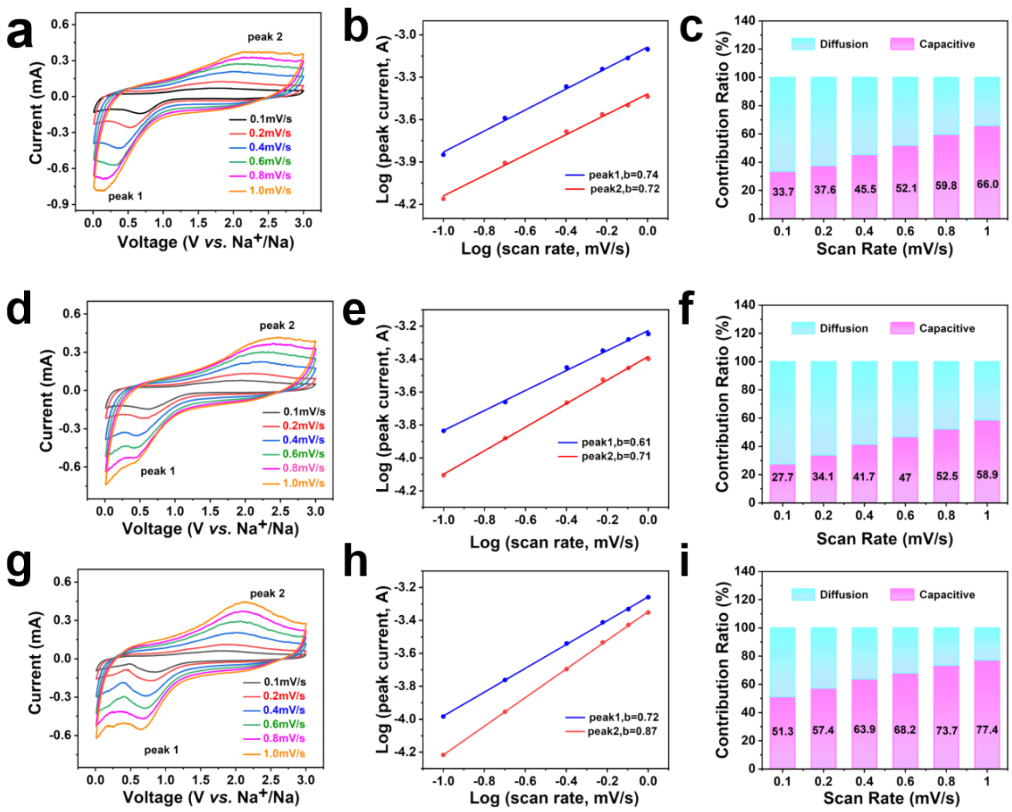

Fig. S6 CV curves, the corresponding plots of log (peak current) vs. log (scan rate) at peak1 and 2, and contribution ratio of capacitive- and diffusion-controlled capacities of the Ni-HHTP sample (a-c), the Ni-HHTP-160 sample (d-f) and the Ni-HHTP-340 sample (g-i).

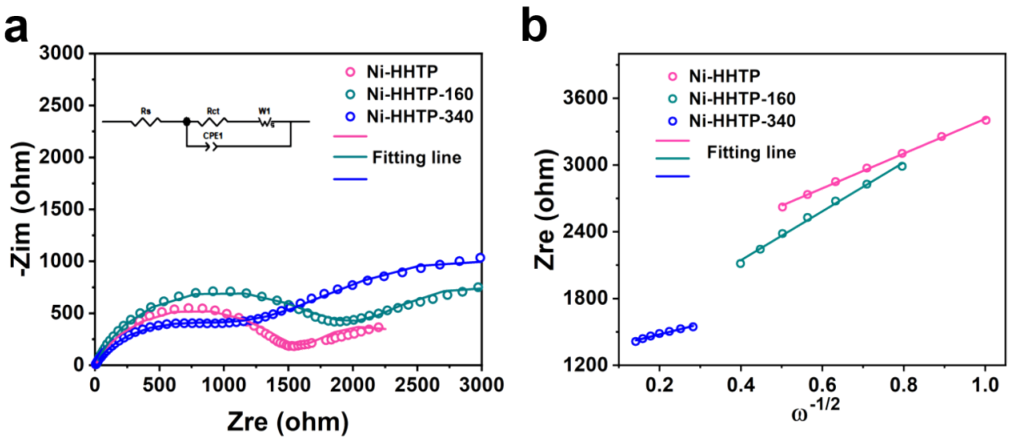

Fig. S7 (a) EIS spectra of the Ni-HHTP sample, the Ni-HHTP-160 sample and the Ni-HHTP-340 sample and equivalent circuit model for EIS fitting. (b) Corresponding Zre vs. $^{-1/2}$ plots in the low frequency region.

The diffusion coefficient of Na^+ ions is calculated by the following equation: [2] (1) $\omega = 2\pi f$, (2) $Zre = R + \sigma\omega^{-1/2}$, (3) $D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}$, Where D represents the diffusion coefficient of the sodium ion, R is the gas constant, T is the absolute temperature, A is the surface area of electrode, n is the number of electrons per molecule during oxidization, F is the Faraday constant, C is the concentration of sodium ion, and σ is the Warburg factor, σ relates to Zre through equation (2) and its value can be obtained from the slope of the lines between Zre and $^{-1/2}$. And then the diffusion coefficient of the sodium ion is calculated and showed in Table S1.

Table S1. D obtained from EIS spectra in Fig. S7 and Fig. 5f.

electrodes	D_{Na^+} ($cm^2\ s^{-1}$)
Ni-HHTP	1.95×10^{-12}
Ni-HHTP-160	9.8×10^{-13}
Ni-HHTP-250	1.52×10^{-11}
Ni-HHTP-340	5.6×10^{-12}

References

1. S. Maiti, A. Pramanik, U. Manju and S. Mahanty, Reversible lithium storage in manganese 1,3,5-benzenetricarboxylate metal-organic framework with high capacity and rate performance, *ACS Appl. Mater. Inter.*, 2015, **7**, 16357-16363.

2. Y. Fang, X. Y. Yu and X. W. D. Lou, Bullet-like Cu_9S_5 Hollow Particles Coated with Nitrogen-Doped Carbon for

Sodium-Ion Batteries, *Angew. Chem. Int. Ed.*, 2019, **58**, 7744-7748.