

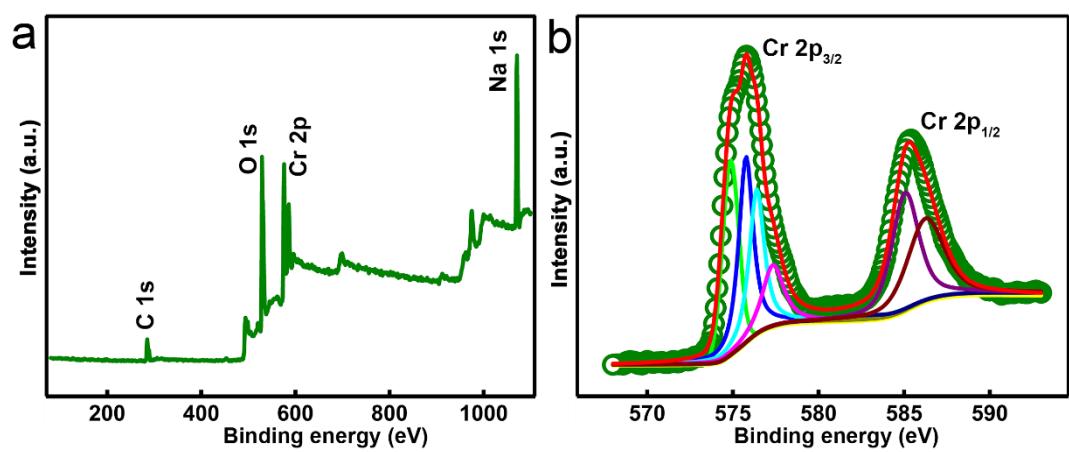
## Supporting Information

### **Comparative investigations of high-rate NaCrO<sub>2</sub> cathodes towards wide-temperature-tolerant pouch-type Na-ion batteries from -15 to 55 °C: Nanowires vs. Bulk**

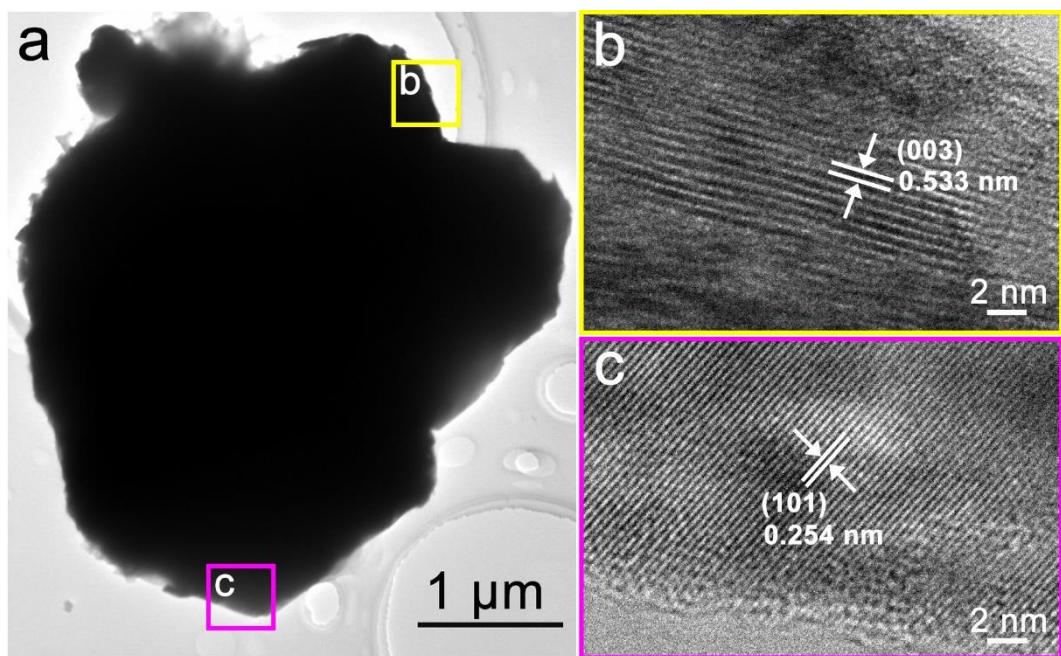
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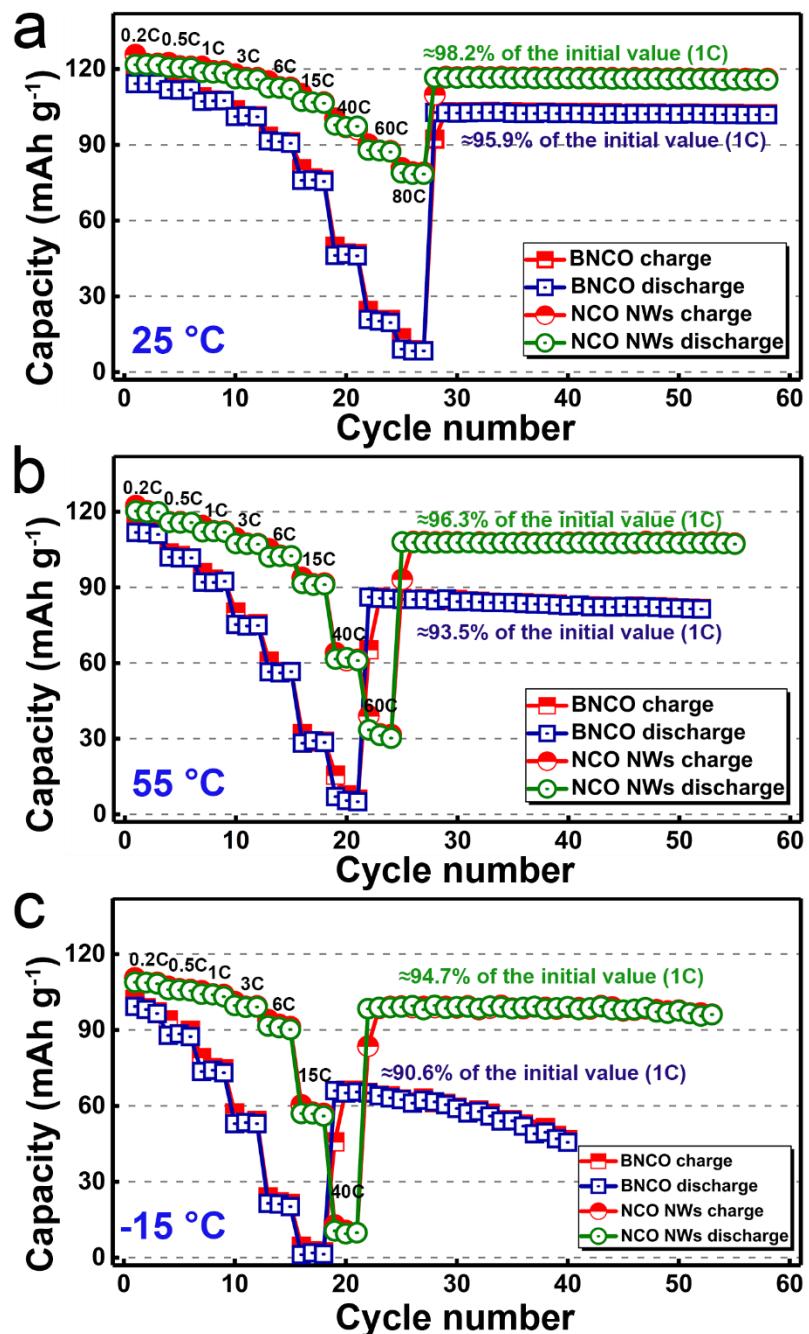
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**Fig. S1** (a) XPS survey and (b) typical high-resolution elemental Cr 2p spectra and corresponding fitting profiles of the NCO NWs

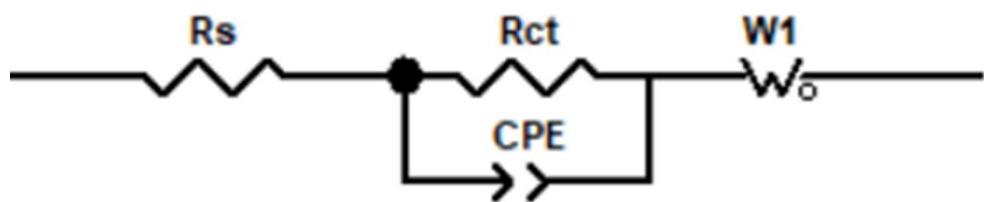


**Fig. S2** (a) TEM and (b-c) HRTEM images of a single BNCO particle. The images in panels (b) and (c) are taken from the yellow and pink rectangle regions in panel (a), respectively

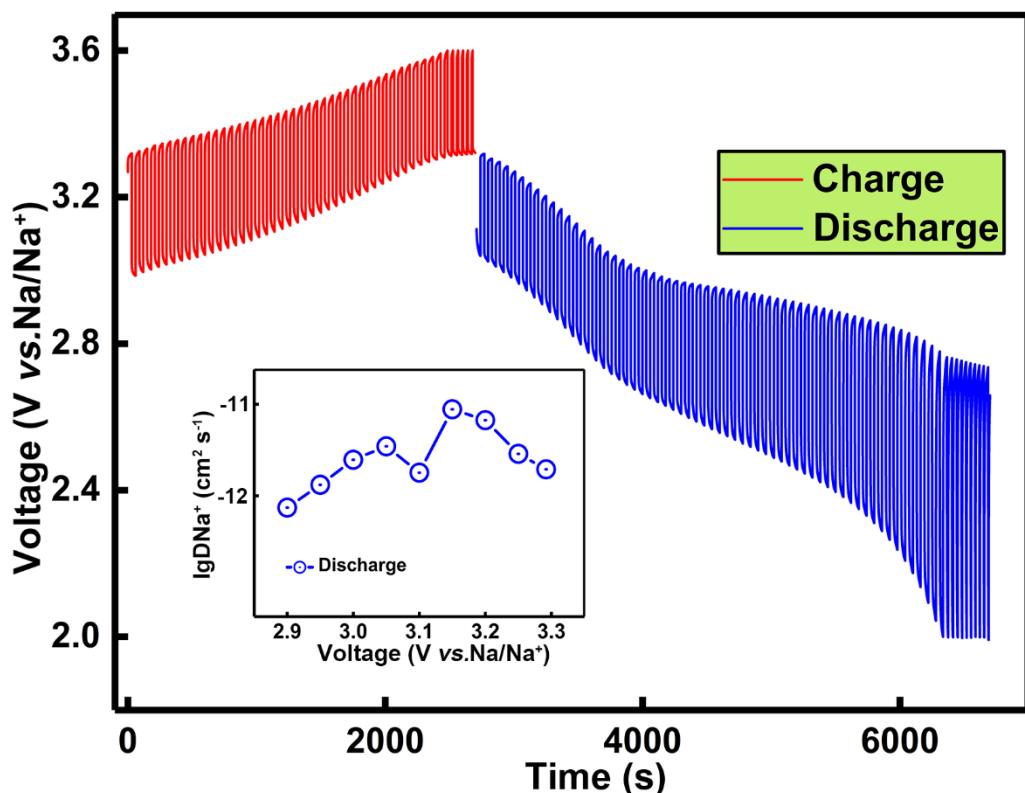


**Fig. S3** Typical rate properties of both BNCO and NCO NWs at various current rates

as indicated (charged/discharged at the same rate) with three cycles per step and then back to 1 C in the voltage of 2.0 – 3.6 V at (a) 25 °C, (b) 55 °C and (c) -15 °C, respectively

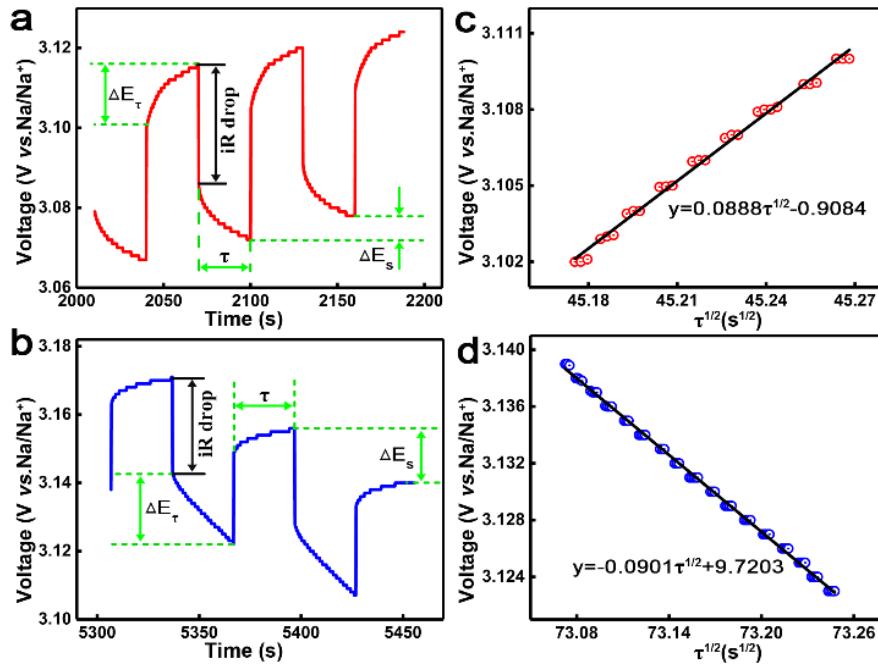


**Fig. S4** Equivalent circuit model used to fit the EIS profiles



**Fig. S5** GITT curves of the BNCO electrode for the charge and discharge process.

The inset is the chemical diffusion coefficient of Na<sup>+</sup> ions as a function of voltage calculated from the GITT curve (after 300 cycles, current density: 2 C)



**Fig. S6** (a) Detailed schematic diagram of a single GITT titration step at ~3.10 V during the charging process and (b) ~3.15 V during the discharging process and (c, d) their corresponding linear behavior of the E vs  $\tau^{1/2}$  relationship of NCO NWs

The calculation of  $D_{Na^+}$  is based on the equation:<sup>1-4</sup>

$$D_{Na^+} = \frac{4}{\pi\tau} \left( \frac{m_B V_m}{M_B S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_\tau} \right)^2 \quad \tau \ll \frac{l^2}{D_{Na^+}}$$

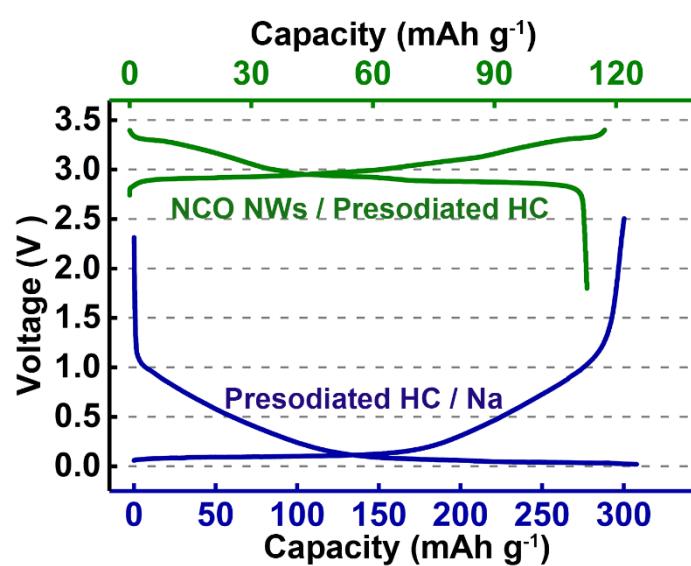
where  $m_B$ ,  $M_B$ ,  $V_m$ ,  $S$  stand for mass, molecular weight, molar volume and surface area of the cathode material respectively.  $\Delta E_s$  and  $\Delta E_\tau$  are the difference between two consecutive stable voltages after relaxation, and the transient voltage-change during a single titration step.

## Reference

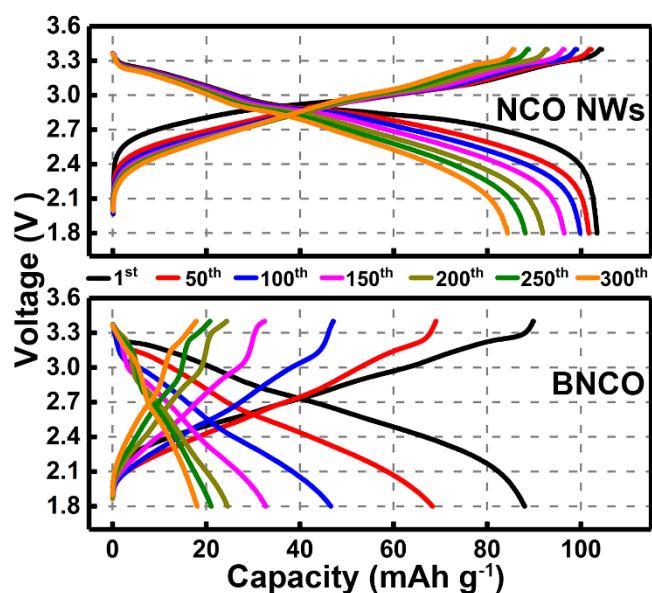
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**Fig. S7** The initial charge/discharge curve at 0.1 C within a potential range of 1.8 – 3.4 V along with the typical charge/discharge profiles of presodiated HC versus Na metal (0 – 2.5 V, 0.1 C)



**Fig. S8** Typical charge–discharge profiles charged 1 C/discharged 2 C rate within a voltage range of 1.8 – 3.4 V at 55 °C for different cycles of the BNCO (the lower) and NCO NWs (the upper) full cells

**Table S1.** Lattice parameters calculated from Rietveld refinement of XRD data of the BNCO

BNCO	
Space group	$R\bar{3}m$
Crystal system	Rhombohedral
$a/\text{\AA}$	2.9743
$b/\text{\AA}$	2.9743
$c/\text{\AA}$	15.9678
$V/\text{\AA}^3$	122.32

**Table S2.** EIS fitted parameters of two samples after different cycles

Samples	Cycles	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$\sigma$ ( $\Omega s^{1/2}$ )
BNCO	50	~3.5	~130.3	—
	100	~3.7	~203.1	~38.2
	200	~4.0	~306.8	~73.9
	300	~4.8	~410.2	—
NCO NWs	50	~3.9	~223.8	—
	100	~4.1	~487.9	~22.8
	200	~4.9	~882.5	~30.2
	300	~7.3	~1543.6	—