Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

# Supporting information

# Single Crystal H-$Nb_2O_5$ Growing Along [001] Crystal Direction for Ultrafast Lithium Storage

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## Experimental Section

**Materials Synthesis:** 3.0 g Nb power (bought from Shanghai aladdin Biochemical Technology Co.,Ltd) was evenly scattered on the combustion boat and place it in the center of a tube furnace. The furnace exposed to ambient air was heated up at a rate of 5 °C min$^{-1}$ to the calcination temperature (1000°C), and it was calcined at 1000 °C for 4 hours, the single-crystalline H-$Nb_2O_5$ was obtained. For preparing the polycrystalline $Nb_2O_5$ BM as the comparison, the sample obtained at 1000 °C was roller milled with zirconium ball for 24h.

## Materials characterization

The phase constitution and purity of the samples were studied by X-ray diffraction (XRD) performed on an Philips X'pert TROMPD [Cu Kα radiation (λ=1.54178 Å)]. Raman spectra were conducted on a Horiba LabRAM HR Evolution system using an Ar laser excitation of 532 nm. The morphologies and microstructures of the samples were observed by field-emission scanning electron microscopy (FESEM, Hitachi SU8010) at 5.0 kV, transmission electron microscopy (TEM), selected area electron diffraction (SAED), and high-resolution TEM (HRTEM, JEM-2100F) at 200 kV. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) measurements were used to confirm the elemental compositions and chemical states of the samples. Electron backscatter diffraction (EBSD) was used to analyze the grain orientation of single-crystalline H-$Nb_2O_5$. Single-crystalline H-$Nb_2O_5$ was prepared by argon ion polishing. The Kikuchi diffraction pattern was collected by Oxford Nordly max3 system equipped with scanning electron microscope. The acceleration voltage was 20 kV, the sample inclination was 69.98°, and the acquisition speed was 137.58 Hz.

## Electrochemical Measurements

The lithium properties of the samples were characterized by assembling CR2032 coin cells in an Ar-filled glove box. The mixture of active material, conductive material (acetylene black) and binder (polyvinylidene fluoride) with mass ratio of $Nb_2O_5$/acetylene black/PVDF = 7:2:1 dissolved in N-methy-I-2-pyrrolidone (NMP) solvent was compressed to the copper foil collector to prepare the working electrode. Dry the electrode in a vacuum oven at 80 °C for 12 h and cut it into a circular shape with the mass loading of 1.5 mg cm$^{-2}$. The lithium metal was used as the counter electrode and the porous polypropylene film as the separator, respectively. The electrolyte was consisting of 1.0 M $LiPF_6$ mixed with a solution of ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 1:1. Aging cells for 12 hours before testing to ensure complete electrolyte penetration into the electrode. The rate and cycling performance of samples were measured on LAND-BT2013A instrument system at the potential range of 1.0–3.0 V versus $Li^+/Li$. The cyclic voltammograms (CV) measurements (1.0-3.0 V) and electrochemical impedance spectroscopy (EIS) measurements (0.01 Hz-100 kHz) were performed using the electrochemical workstation (CHI660E). The galvanostatic intermittent titration technique (GITT) experiments were carried out at a current density of C/10 with a current pulse width of 0.5 h.

The energy/power density of lithium ion capacitor can be obtained by the following equation:

$$E = \int_{t1}^{t2} IV(t)dt \quad (1)$$

$$P = \frac{E}{t} \quad (2)$$

Where $I$ (A $g^{-1}$) is the constant current density based on the total active materials, $V$ (V) is the working voltage, $t_1$ and $t_2$ is the discharge start/end time (s), and $t$ (s) is the discharging time of lithium ion capacitor. $E$ is the energy density and $P$ is the power density.

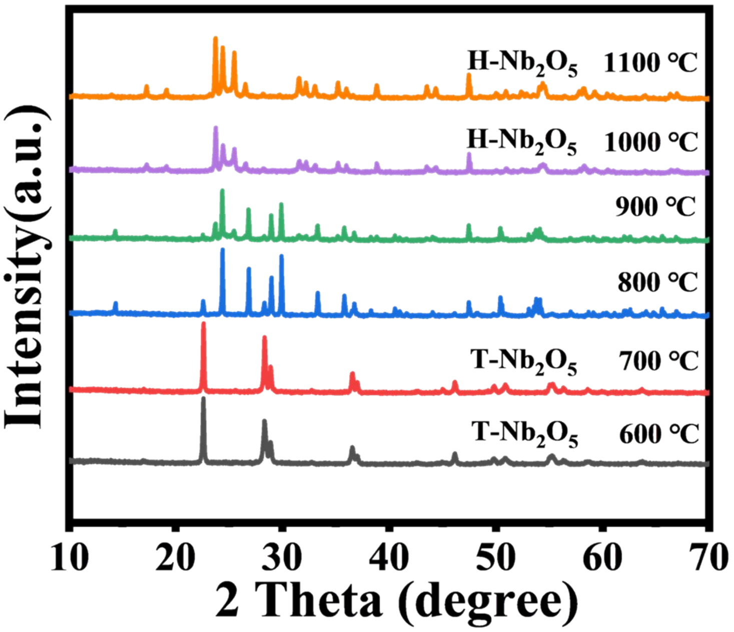


Fig. S1 High resolution XRD patterns of the products by oxidizing the Nb powder precursor at 500, 600,700,800,900,1000,1100 °C.

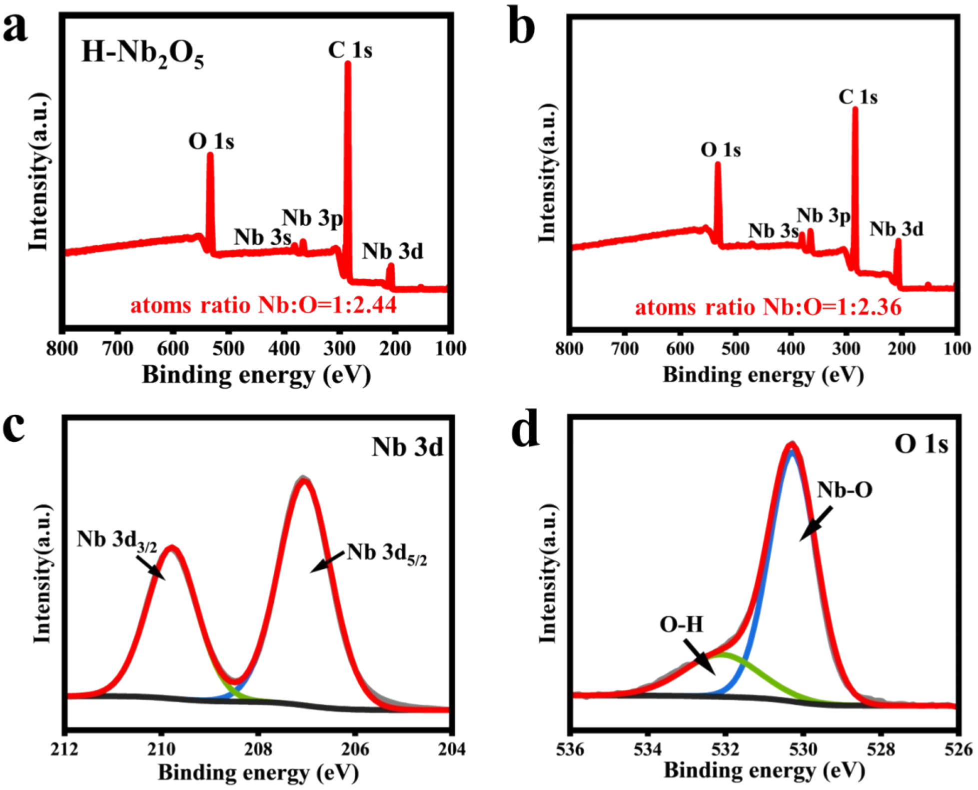


Fig. S2 (a) The survey XPS of wide H-$Nb_2O_5$. (b) The survey XPS of wide $Nb_2O_5$ BM. (c)(d) High-resolution Nb 3d and O 1s XPS spectra of $Nb_2O_5$ BM.

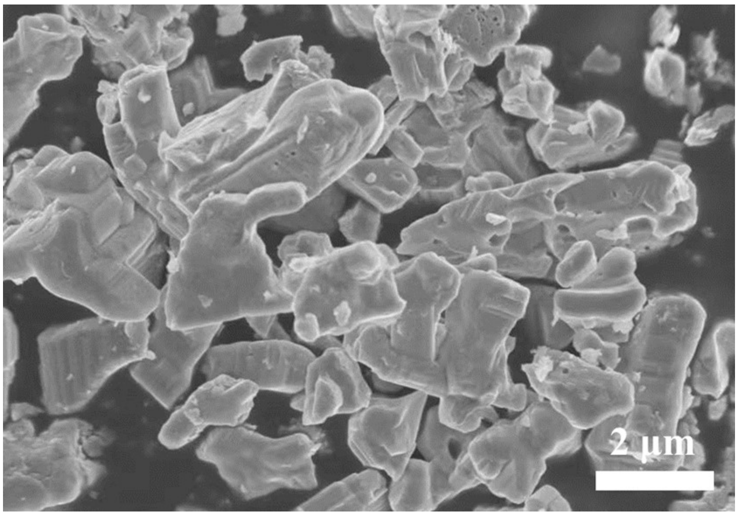


Fig. S3 SEM image of H-$Nb_2O_5$ at low magnification.

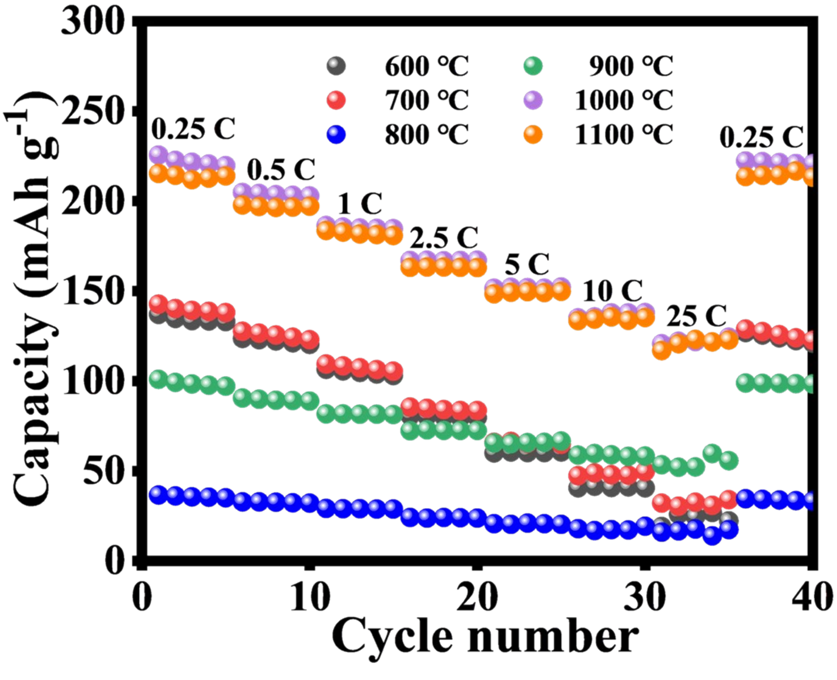


Fig. S4 Rate performances of the products by oxidizing the Nb powder precursor at 500, 600,700,800,900,1000,1100 °C at various current densities.

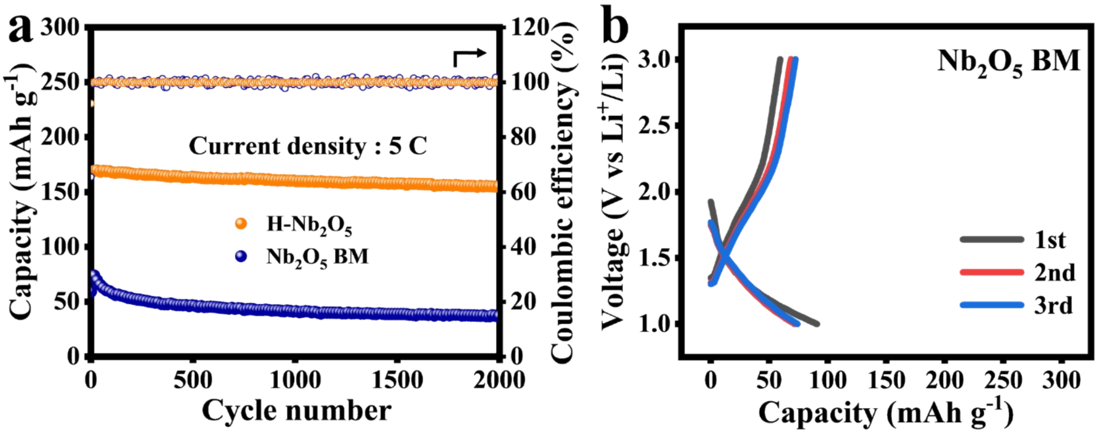


Fig. S5 (a) Cycling performances of H-$Nb_2O_5$ and $Nb_2O_5$ BM tested at a low current density of 5 C.(b) The galvanostatic charge discharge (GCD) measurements of the first three cycles for $Nb_2O_5$ BM at 0.5 C.

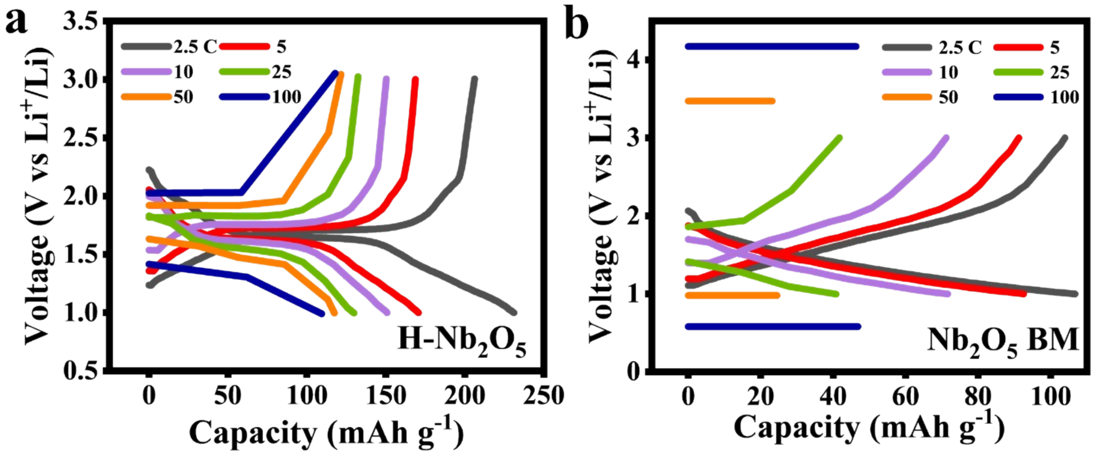


Fig. S6 (a)(b) The charge-discharge curves of H-$Nb_2O_5$ and $Nb_2O_5$ BM at various rates (from 2.5 C to 100 C).

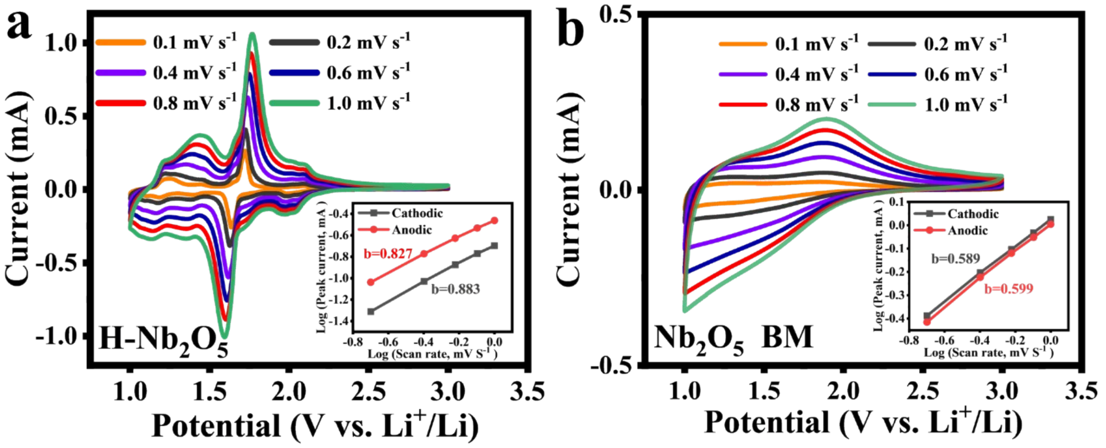
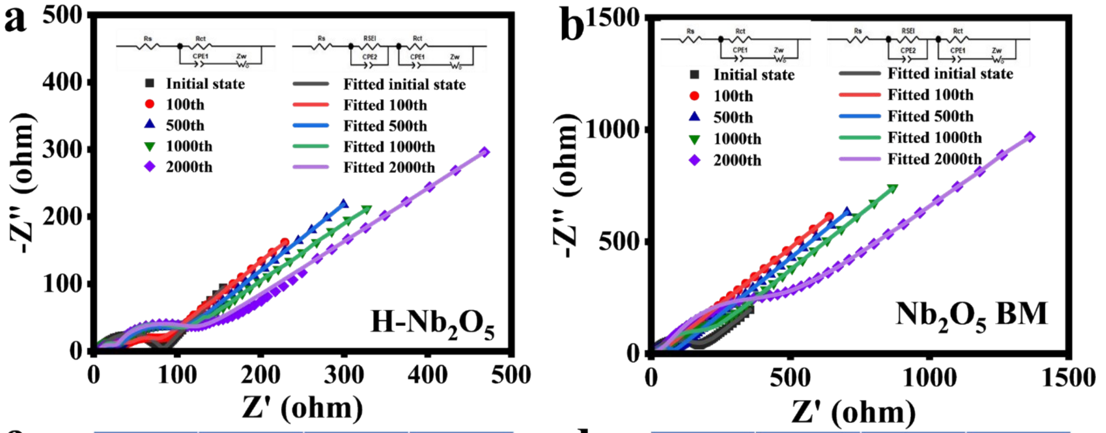


Fig. S7 (a)(b) The CV curves at different scan rates of 0.1-1.0 mV s$^{-1}$ of H-$Nb_2O_5$ and $Nb_2O_5$ BM (inset: corresponding parameter *b* was calculated for the slope of the log *i*(*V*) -log *v* linear graph).



c

| | $R_s(\Omega)$ | $R_{SEI}(\Omega)$ | $R_{ct}(\Omega)$ |
|---|---|---|---|
| 0th | 5.72 | | 71.26 |
| 100th | 6.37 | 20.73 | 41.15 |
| 500th | 7.51 | 28.38 | 43.01 |
| 1000th | 8.51 | 32.52 | 48.12 |
| 2000th | 3.56 | 36.62 | 57.75 |

d

| | $R_s(\Omega)$ | $R_{SEI}(\Omega)$ | $R_{ct}(\Omega)$ |
|---|---|---|---|
| 0th | 6.72 | | 123.80 |
| 100th | 7.90 | 31.86 | 55.03 |
| 500th | 8.27 | 37.38 | 78.30 |
| 1000th | 9.17 | 45.52 | 118.68 |
| 2000th | 7.61 | 52.62 | 183.20 |

Fig. S8 (a)(b) The electrochemical impedance spectroscopy (EIS) of H-$Nb_2O_5$ and $Nb_2O_5$ BM. (c)(d) The EIS fitting data of H-$Nb_2O_5$ and $Nb_2O_5$ BM.

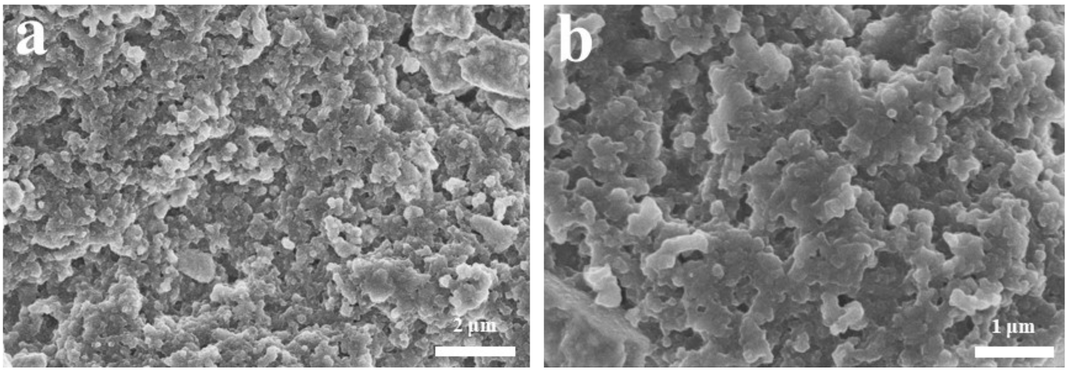


Fig. S9 SEM images of $Nb_2O_5$ BM after 2000 cycles at 5 C.

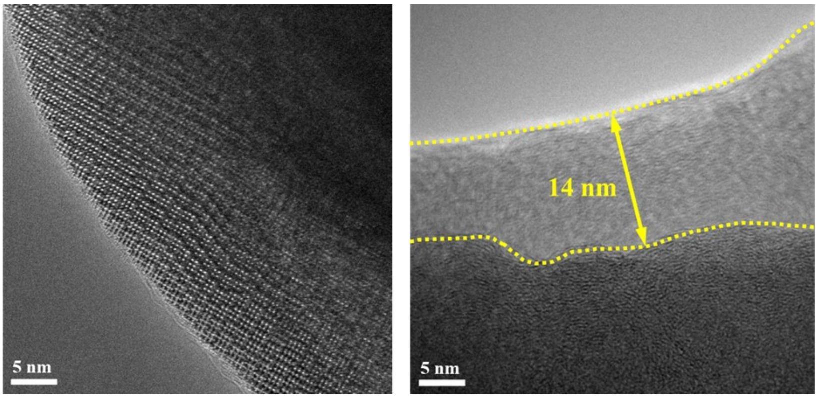


Fig. S10 (a)(b) HRTEM images of $Nb_2O_5$ BM before and after 2000 cycles at 5 C.

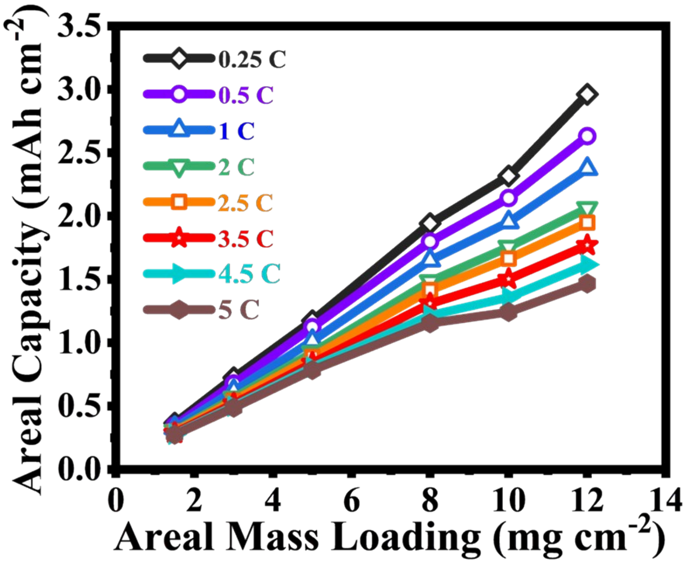


Fig. S11 The correlation of areal capacity with mass loading (1.5 to 12 mg cm$^{-2}$) at various rates for the H-$Nb_2O_5$.

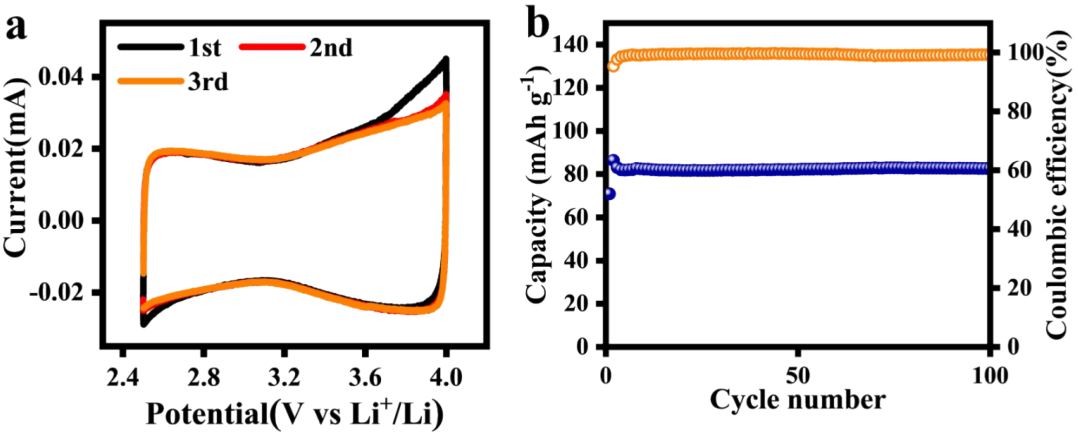


Fig. S12 (a) The initial three CV curves of AC. (b) Cycle performance of AC at 0.5 C.