Supporting Information

In situ composite solid electrolyte interphases (SEI) with regulated sodium ion flux enable dendrite-free, long-cycle sodium metal batteries.

1. Experimental Section

Synthesis of N-fluorobenzoyl-N'-phenylthiourea (FBT): A 1:1 weight ratio of 4-fluorobenzoylhydrazine and phenyl isothiocyanate was added to a ball mill jar, followed by an appropriate amount of ethanol. The mixture was then balanced with ball mill beads and ball-milled at a speed of 600 revolutions per minute for 10 hours. After the milling process, the beads were removed, and the sample was heated in a vacuum oven at 90°C for 12 hours to ensure complete evaporation of ethanol.

Preparation of FBT-Sodium Metal Composite Anode (FBT-Na): The prepared FBT was dissolved in tetrahydrofuran (THF) to create FBT-THF solutions with mass fractions of 1%, 2%, 3%, and 4% (4% being the maximum solubility of FBT in THF). The solutions were shaken to ensure complete dissolution. Under an argon atmosphere with water and oxygen levels below 0.05 ppm in a glove box, 40 mL of FBT-THF solution was uniformly drop-cast onto 12 mm diameter sodium metal discs. The discs were then dried on a heating plate at 90°C for 12 hours to ensure complete evaporation of THF.

Assembly of Symmetric Cells: Conducted in an argon-filled glove box, the cells utilized polyethylene (PE) separators and 75 μL of sodium hexafluorophosphate dissolved in 100% diethoxyethane as the electrolyte. The cells were assembled in the order of negative can, sodium disc, separator, electrolyte, sodium disc, spacer, spring, and positive can, and then sealed under a pressure of 50 psi.

Assembly of Sodium-Copper Asymmetric Cells: Copper discs of 12 mm were cut from copper foil and immersed in a solution of alcohol with a few drops of HCl. After ultrasonication for 30 minutes, the copper discs were removed and dried for later use. The sodium-copper cells were assembled in the argon-filled glove box with PE separators and electrolyte consisting of sodium hexafluorophosphate dissolved in 100% diethoxyethane. The assembly procedure was the same as described above, with the exception that the sodium disc on the positive side was replaced with a copper disc.

Assembly of Full Cells: $Na_3V_2(PO_4)_3$ (NVP) was used as the cathode, and the slurry was composed of 80 wt% NVP, 10 wt% polyvinylidene fluoride (PVDF) binder, and 10 wt% Super P. The diameter of the cathode discs was 12 mm. The assembly order was the same as described above, with the sodium disc on the positive side being replaced with an NVP cathode disc.

All samples, including 4-fluorobenzoylhydrazine, phenyl isothiocyanate, sodium discs, and electrolyte, were purchased from Duoduo Reagent Network without any further treatment.

Material Characterization: The morphology of the samples was characterized using a JEOL JSM-7500F field-emission scanning electron microscope (SEM) with an acceleration voltage of 3.0 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermo ESCALAB 250 spectrometer with non-monochromatic Al Kα X-rays as the excitation source, using the C1s peak (284.8 eV) as the reference line.

Electrochemical Testing Methods: CR2032 coin cells were assembled in an argon-filled glove box with water and oxygen levels maintained below 0.05 ppm. A Neware (CT-4800) battery testing system was used for room temperature constant current charge-discharge performance testing of symmetric cells. Additionally, the same Neware (CT-4800) system was used to evaluate the constant current charge-discharge performance of full cells at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI660D electrochemical workstation with a frequency range of 100 kHz to 0.01 Hz and an amplitude perturbation of 10 mV. Cyclic voltammetry (CV) and Tafel tests were conducted on a CHI660 electrochemical workstation with a scanning range of -0.2 V to 0.2 V and a scan rate of 10 mV/s.

2. Supplementary Figures

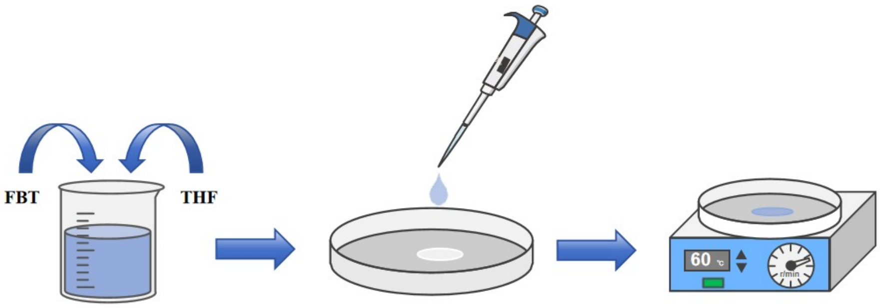

Figure S1. Schematic illustration of the preparation process for the FBT-Na electrode.

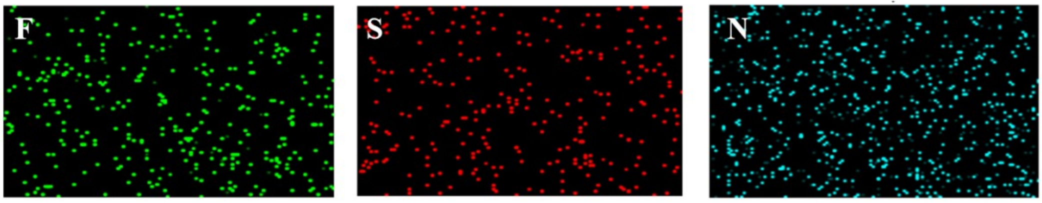

Figure S2. EDX spectroscopy of the FBT-Na electrode surface after 50 cycles.

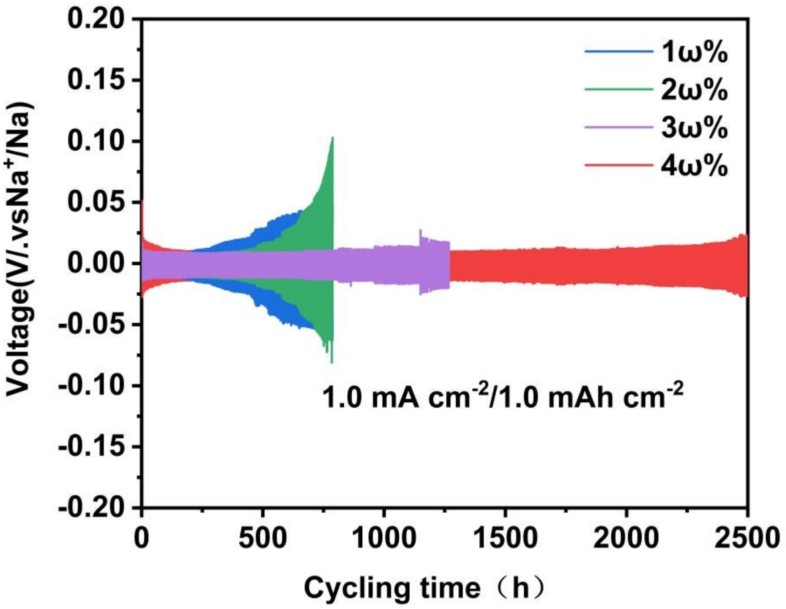

Figure S3. Comparative cycling performance of FBT-Na symmetric batteries fabricated from FBT-THF solutions of varying concentrations.

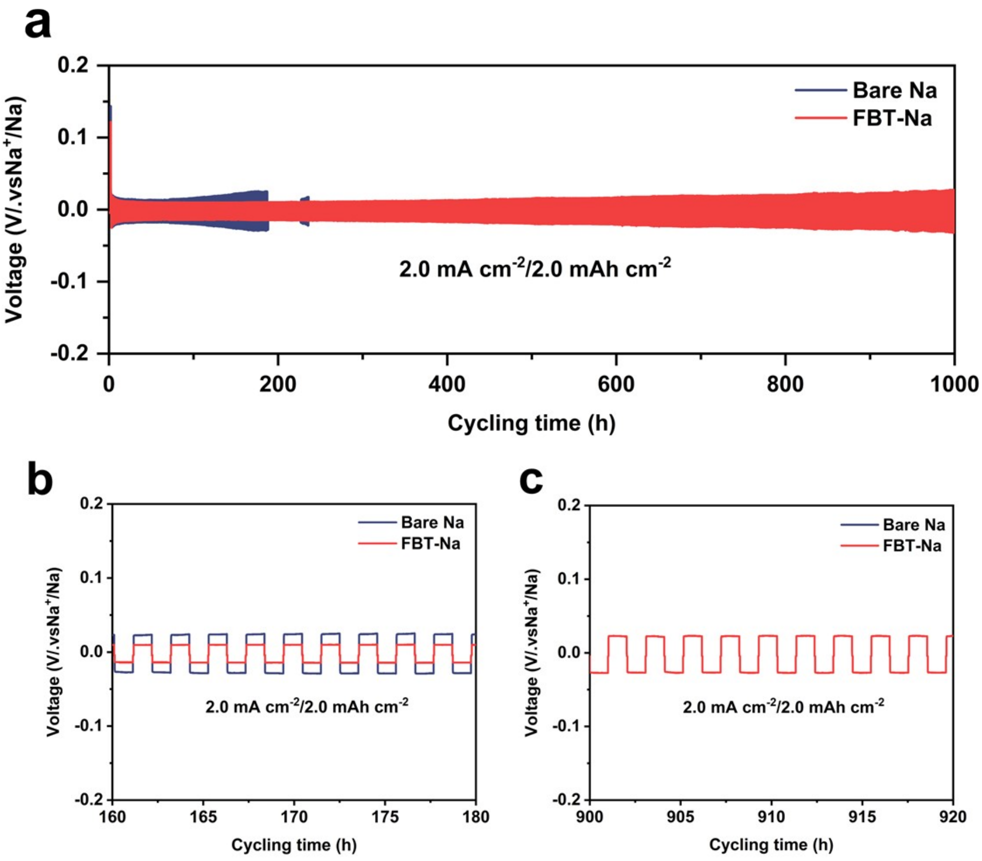

Figure S4. a-c) Cycling performance of Bare Na and FBT-Na symmetric batteries at 2.0 mA cm^{-2}/2.0 mAh cm^{-2}, along with magnified views of specific time intervals.

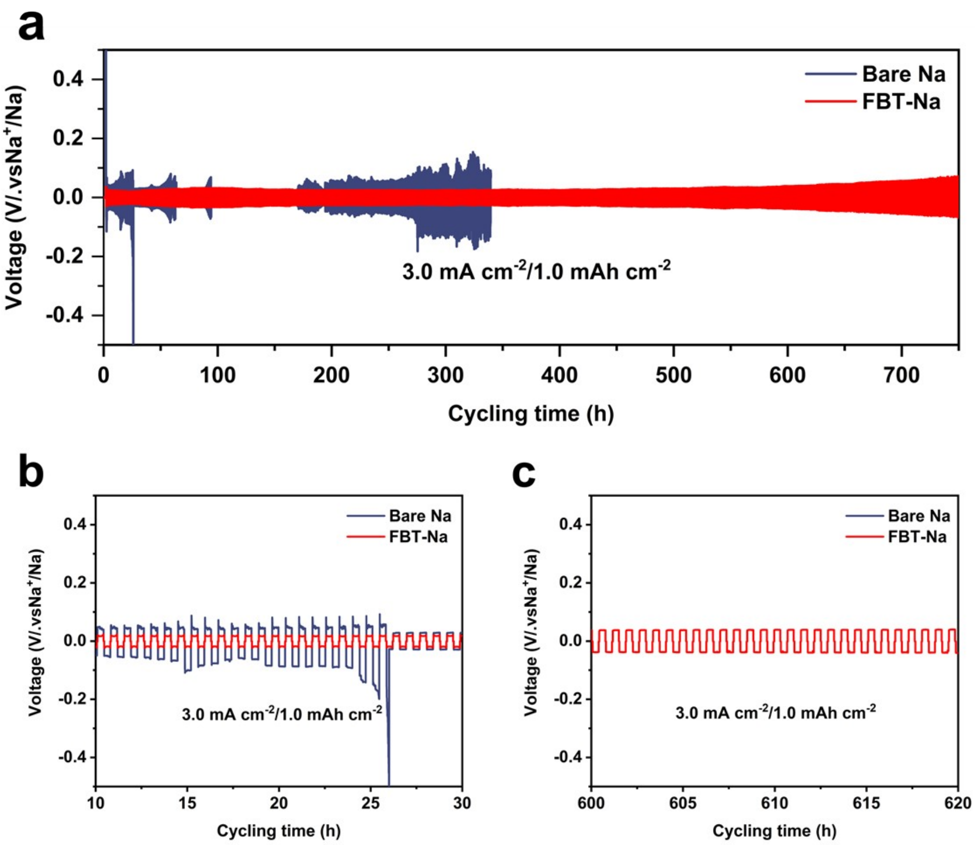

Figure S5. a-c) Cycling performance of Bare Na and FBT-Na symmetric batteries at 3.0 mA cm^{-2}/1.0 mAh cm^{-2}, along with magnified views of specific time intervals.

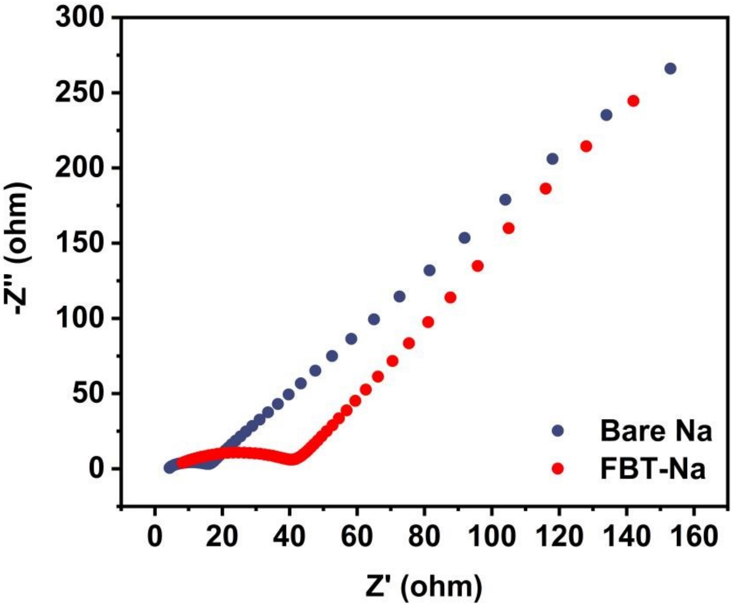

Figure S6. Impedance plots of Bare Na||Cu and FBT-Na||Cu cells before cycling.

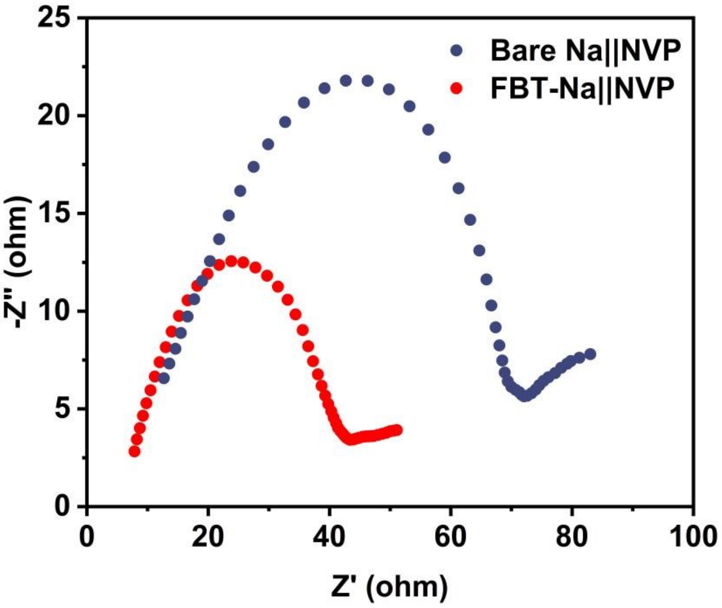

Figure S7. Impedance plots of Bare Na||NVP and FBT-Na||NVP cells before cycling.