Quasi-Zero-Strain Layered $Nb_4P_2S_{21}$ Cathode for High-energy Solid-State Polymer Na-Metal batteries

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Experimental section

Synthesis of $Nb_4P_2S_{21}$ cathode materials: $Nb_4P_2S_{21}$ is synthesized by the solid-state reaction from a stoichiometric pure element in a flame-sealed quartz tube. After annealing at 700 C°, the brown powder of $Nb_4P_2S_{21}$ sample was collected.

Solid polymer electrolyte preparation: 3 M $NaPF_6$ (≥99.9%, DoDochem) was added into DME (97%, DoDochem), Then, the 3 M $NaPF_6$ in DME was mixed with DOL

(≥99.9%, DoDochem) (1:1 wt.%) to gain the LE. The solution was used on cells and stood for 3 days to complete the gelation process. All process was finished in the glove box (H_2O < 0.1 ppm, O2 < 0.1 ppm).

Material characterization: X-ray diffraction patterns of $Nb_4P_2S_{21}$ samples were obtained on a Bruker D8 Advance diffractometer equipped with mirror-monochromatic Cu Kα radiation (λ = 0.15406 nm) at a scan rate of 10˚ min^{-1} with 2θ from 10˚ to 60˚. The *in-situ* XRD spectra were obtained on a live discharge/charge process in a cell purchased from Bejing Scistar Technology *Co. Ltd.* The morphology of $Nb_4P_2S_{21}$ was investigated by a JEOL (JSM6510) scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDXS, Oxford Instruments) and transmission electron microscopy (FEI Tecnai F20, USA). Raman spectra was obtained from a Jobin-Yvon LabRAM HR-800 spectrometer with a laser excitation at 532 nm. The High-resolution XPS spectra were obtained from an X-ray photoelectron spectrometer (XPS, Thermo Scientific, ESCALAB 250, USA).

Electrochemical characterization: The composite electrodes were fabricated from the active materials $Nb_4P_2S_{21}$ powder (80 wt%), super P (10 wt%), and sodium alginate (SA) binder, and deionized water was used as a solvent to get a slurry. Then the slurry was coated evenly on a copper foil using a blade with a mass loading of ~1.8 mg cm^{-2}. The electrode was then dried in a vacuum oven at 80 °C for 8 h. The half cells were assembled in coin-type cells (MTI corporation-CR2032) within an Ar gas-filled glove box. A piece of sodium was utilized as the counter electrode. Glass fiber was utilized as a separator. A CHI1760e electrochemical workstation was used for the cyclic voltammetry (CV) tests with a potential range between 3 V and 1 V at different scan rates. A Land CT2001A tester (Wuhan, China) was applied to get the galvanostatic cycling performance and the GITT voltage profile of the assembled cells with a cutoff voltage between 3 V and 1 V at room temperature. Electrochemical impedance spectroscopy (EIS) was also tested with a CHI1760e electrochemical workstation at the frequency of 0.1 to 10000 Hz.

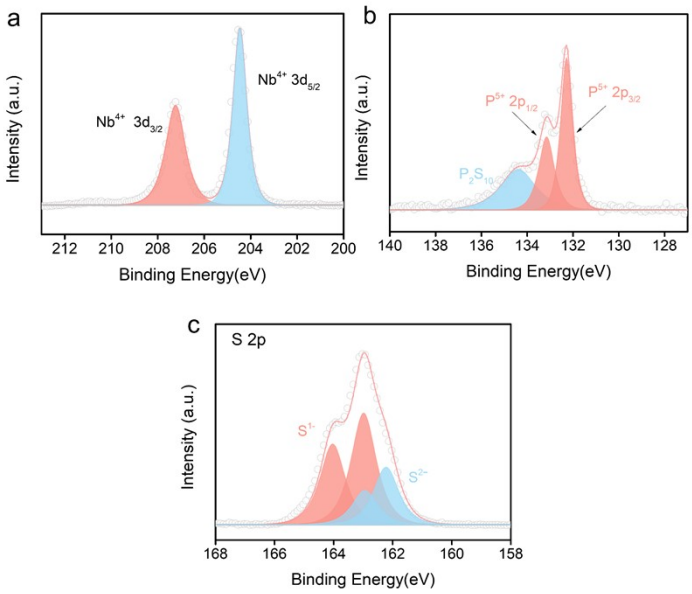

Fig. S1 (a-c) High-resolution XPS spectra of Nb, P, and S.

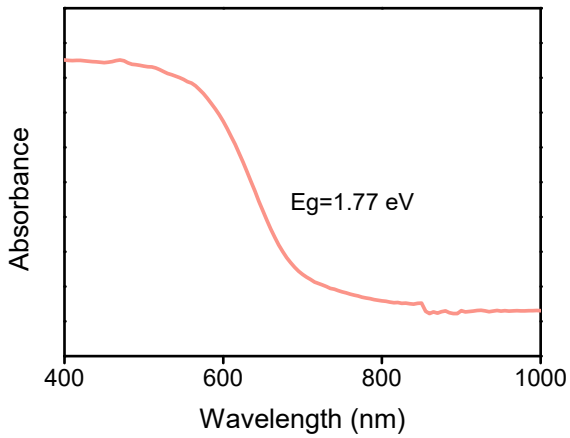

Fig. S2 UV-vis spectrum of $Nb_4S_2S_{21}$.

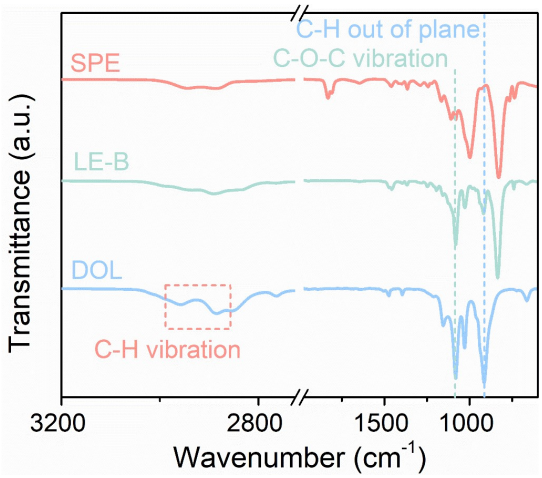

Fig. S3 FT-IR spectra of DOL, LE, and SPE.

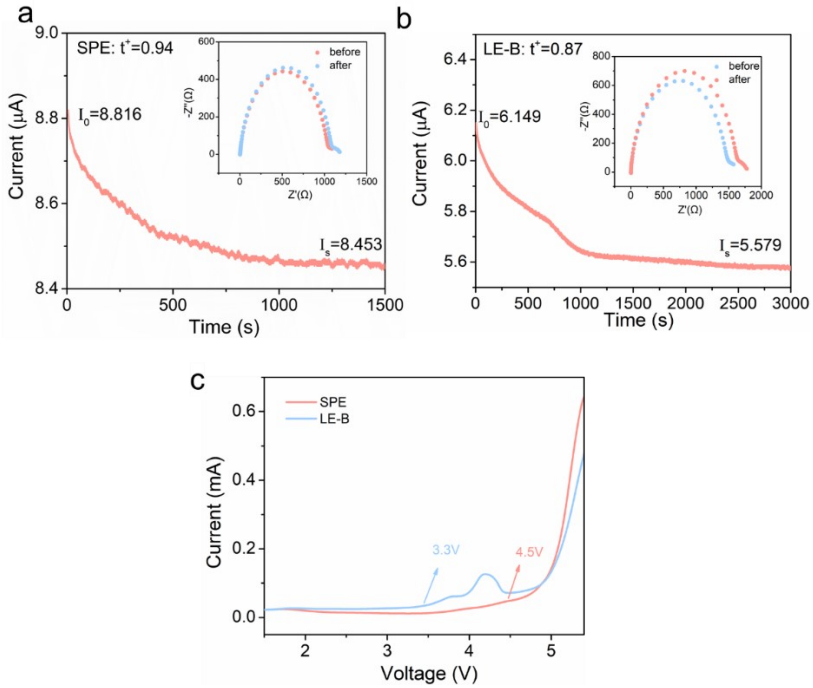

Fig. S4 (a-b) Chronoamperometry curve of Na|Na cell in SPE and LE-B under a polarization voltage of 10 mV. (c) Linear sweep voltammetry with a scan rate of 5 mV s^{-1} from 0 to 5 V.

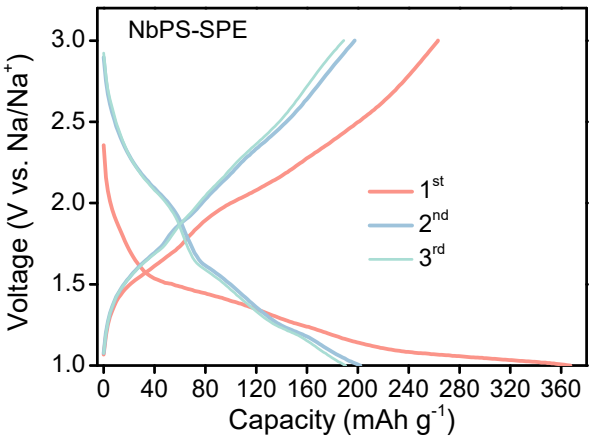

Fig. S5 GCD curves of NbPS-SPE at initial three cycles.

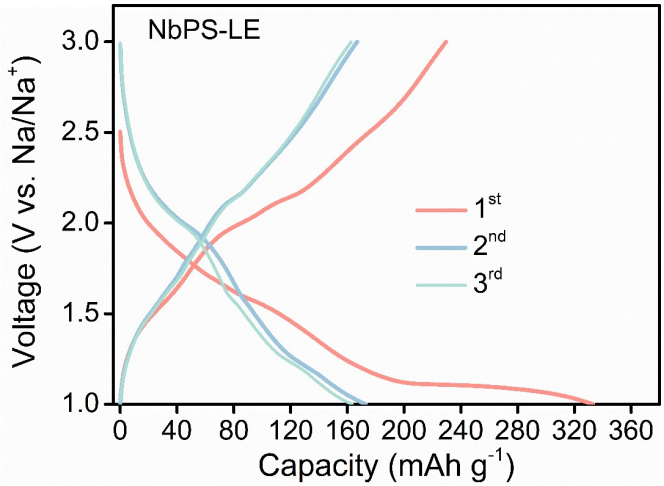

Fig. S6 GCD curves of NbPS-LE at initial three cycles.

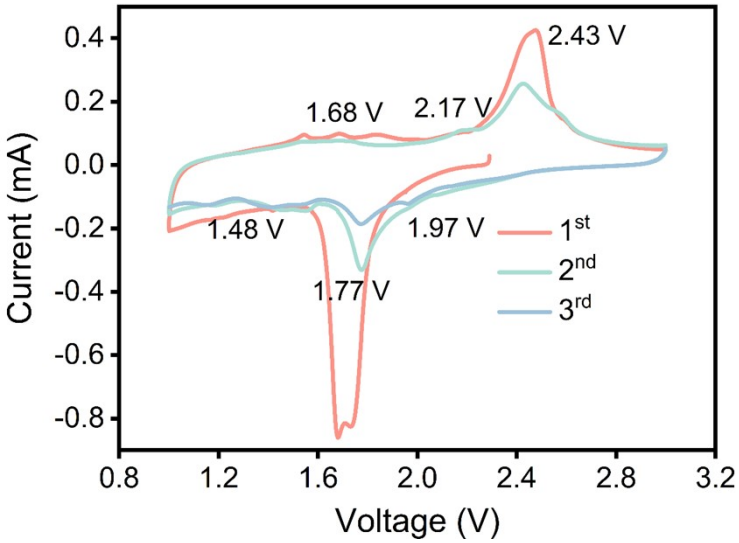

Fig. S7 CV curves of $Nb_4P_2S_{21}$ cathode in liquid electrolyte.

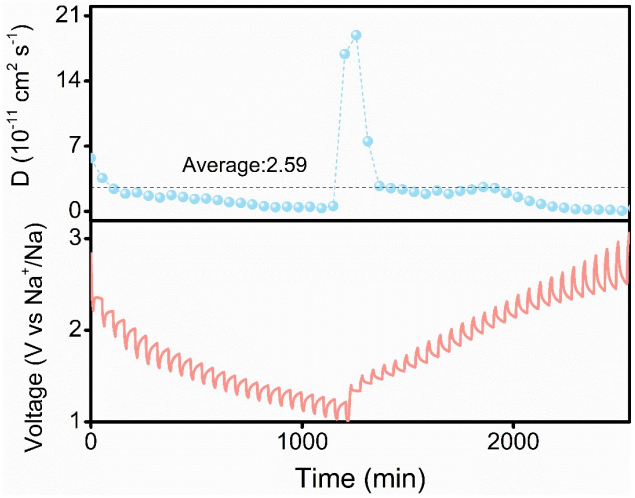

Fig. S8 GITT potential of $Nb_4P_2S_{21}$ in the second cycle in LE.

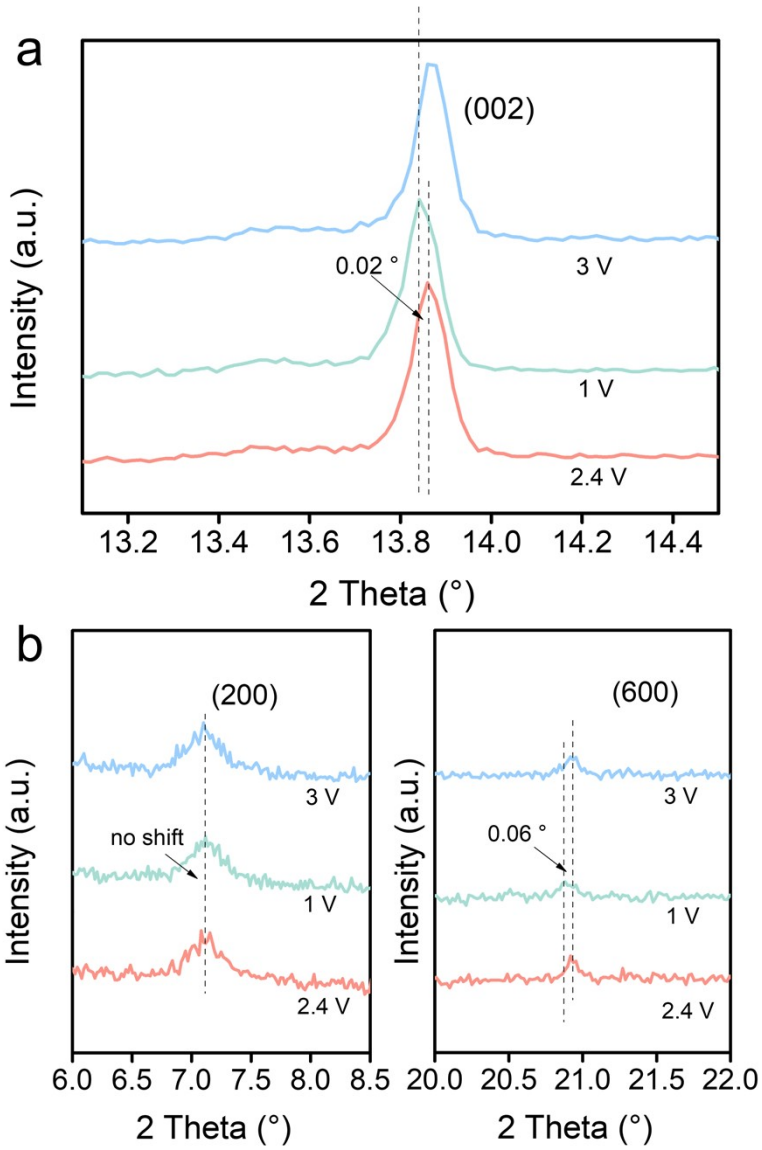

Fig. S9 Shift of XRD peaks during the discharging/charging process. (a) (002) plane, (b) (200), and (600) plane.

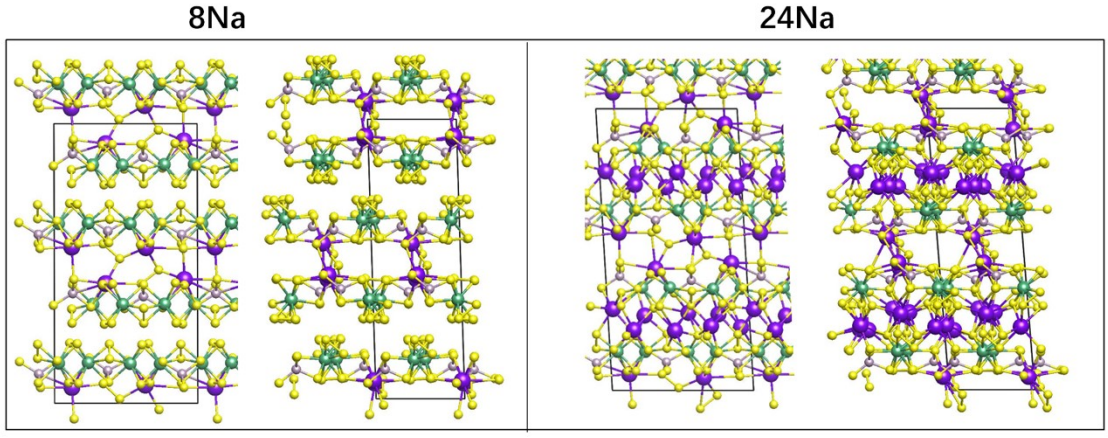

Fig. S10 Na^+ intercalation model in $Nb_4P_2S_{21}$.