Electronic Supplementary Information for

A zero-strain insertion cathode material of nickel ferricyanide for sodium-ion batteries

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Experimental section

Synthesis of NiFe-PBA Nanoparticles

2 m mol $K_3Fe(CN)_6 \bullet 10H_2O$ was dissolved in 100 mL of deionized water to form solution A, and 2 m mol $Ni(NO_3)_2 \bullet 9H_2O$ was dissolved in 10 mL of deionized water to form solution B. Solution B was slowly added to solution A to form a yellow precipitate. After aging for 12 h, the composite was collected by centrifugation, washed by water and ethanol three times, and then dried at 100 °C overnight.

Structural characterization

Scanning electron microscope (JEOL 6701F, operated at 10 kV) was used to visualize the morphology and size of the as-prepared products. X-ray diffraction measurements were carried out using a Rigaku D/max-2500 with filtered Cu Kα radiation ($\lambda = 1.5405$ Å) operated at 40 kV and 200 mA. The chemical composition was examined by an elemental analyzer (Flash EA 1112) for C, H, and N elements and inductively coupled plasma atomic emission spectroscopy on a Shimazu ICPE-9000 for Fe, Ni, and K elements. Raman spectra were obtained using a DXR from Thermo Scientific with a laser wavelength of 532 nm. Thermogravimetric analysis was conducted on a TG/DTA6300 instrument at a heating rate of 2 °C min^{-1} under N_2 environment with a flow rate of 200 mL min^{-1}.

Electrochemical characterization

Electrochemical experiments were carried out in two-electrode Swaglok-type cells assembled in an argon-filled glove box. To prepare working electrodes of these batteries, a mixture of NiFe-PBA powder, carbon black and poly (vinyl difluoride) (Aldrich) at 8:1:1 weight ratio was coated onto an Aluminum foil (99.6%; Goodfellow). Na (Li) foil with a diameter of 10 mm was used as counter electrode, and porous glass fiber (GF/D) from Whatman was used as separator. 1 M $NaPF_6$ ($LiPF_6$) was dissolved in a mixture of propylene carbonate (PC) and ethylene carbonate (EC) at 1:1 volume ratio to be used as electrolyte (Aldrich). Galvanostatic tests were carried out using an Arbin BT2000 system within the voltage range of 2.0–4.1 V (vs Na^+/Na) or 2.3–4.4 V (vs Li^+/Li). Cyclic voltammetry measurements were performed on an Autolab PG302N at a scan rate of 0.1 mV s^{-1} within the potential range of 2.0–4.7 V (vs Na^+/Na).

Ex situ characterization

Swagelok-type cells in charged or discharged states were disassembled in the glove box. To remove residual electrolyte, cathode electrodes were taken out of the cell and washed five times. The electrode plates were transferred to some specially designed devices for *ex situ* XRD or Raman observation. The electrode plates were sealed in argon, and a vacuum transfer sample stage was used to protect the sample from being exposed to air.

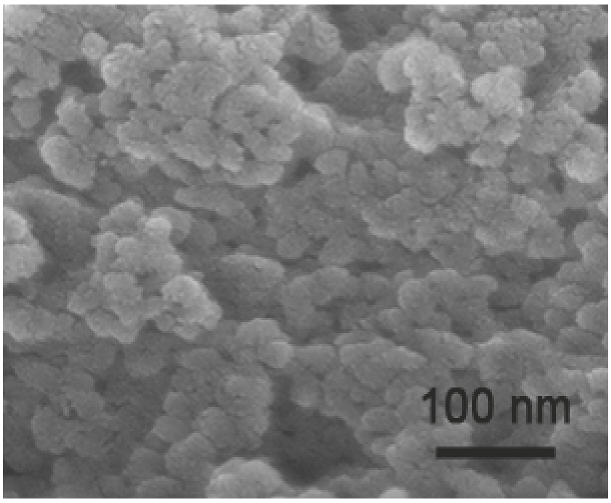

Fig. S1 High-resolution SEM image of NiFe-PBA.

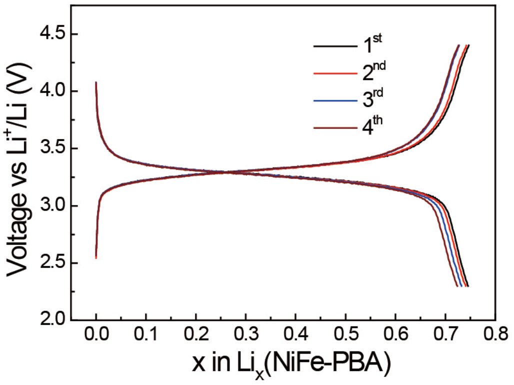

Fig. S2 Galvanostatic charge/discharge voltage profiles of NiFe-PBA/Li cells under a current density of 20 mA g^{-1}.

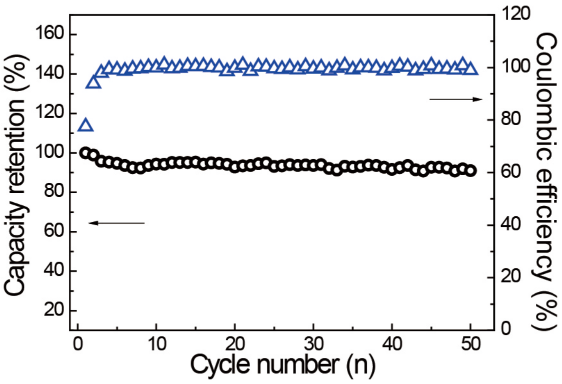

Fig. S3 Cycling performance of the NiFe-PBA/Li cells cycled under 20 mA g^{-1} between the voltage limits of 2.3 V and 4.4 V (vs Li^+/Li). Triangles show the corresponding Coulombic efficiencies.

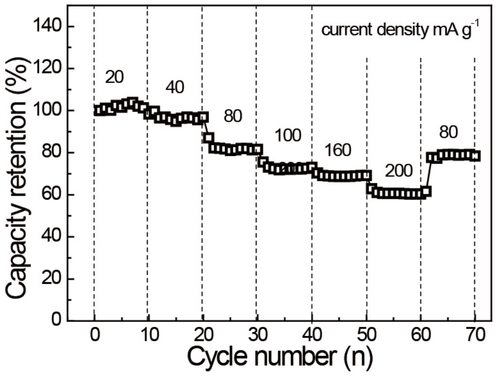

Fig. S4 Rate capability of NiFe-PBA between the voltage limits of 2.0 V and 4.1 V (vs Na^+/Na).