Supporting Information

Sodium Storage Mechanism of GeP_5/C Composite as High Capacity Anode Material for Sodium-ion Batteries

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Experimental methods

1. Material synthesis

GeP_5 powder was prepared by mixing Ge powder and red P (RP) powder in a mole ratio of 1:5 for 6 h at 1200 rpm in a high-energy ball mill. The ball-to-weight ratio was about 20:1. The RP phase can be changed into black P (BP) phase during the ball milling process. To prepare GeP_5/C composite, the as-prepared GeP_5 powder and super P were mixed in a mass ratio of 7:3, and then mixed for 4 h at 1200 rpm. The steel vial was assembled in an argon-filled glove-box ($O_2 \leq 0.3$ ppm, $H_2O \leq 0.5$ ppm) to make sure the milling process under inert atmosphere.

2. Characterization

The crystal structure of the as prepared samples was characterized using the X-ray diffractometer with a Cu-Kα source ($\lambda = 0.1540$ nm). The microstructure of the samples was characterized by filed emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Ge K-edge X-ray absorption spectroscopy (XAS) was performed at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF). The AUTOBK code was used to normalize the absorption coefficient, and separate the extended X-ray absorption fine structure (EXAFS) signal, $\chi(k)$, from the isolated atom absorption background. The extracted EXAFS signal, $\chi(k)$, was weighted by k^3 to emphasize the high-energy oscillations and then Fourier-transformed in a k range from 3.2 to 10.3 °$Å^{-1}$ using a Hanning window with a window sill (Δk) of 1.0 $Å^{-1}$, thereby obtaining magnitude plots of the EXAFS spectra in R-space (Å). PDF data were collected at beamline 28-ID-2 of NSLSII (BNL) with an incident photon wavelength of 0.1877 Å and an amorphous silicon area detector (Perkin-Elmer) to obtain data to large momentum transfer values. The collected raw images were radially integrated using Fit2D software. PDFgetX3 software was used to correct the data for background contributions, Compton scattering and detector effects, and to Fourier transform ($Q_{max} = 22.5$ Å) the data to generate G(r) and the PDF.

3. Electrochemical measurements

The electrochemical measurements were performed by using 2032-coin cells. The working electrode was prepared by mixing the GeP_5/C powder, super P (conductive agent), and polyacrylic acid sodium salt (Na-PAA, binder) at the weight ratio of 7:2:1 in distilled water to form the slurry and then pasted onto the copper foil, followed by drying at 70 ^oC overnight in the vacuum oven. The electrolyte was 1.0 M $NaClO_4$ dissolved in ethylene carbonate-diethyl carbonate (EC-DEC, 1:1 by volume) with 5 vol. % addition of fluoro-ethylene carbonate (FEC). The sodium foil was used as both counter electrode and reference electrodes. The cells were assembled in an argon-filled glove box. The galvanostatic discharge and charge tests and cyclic voltammetry (CV) tests were carried out on a Land CT2001A battery test system and CHI660 system, respectively.

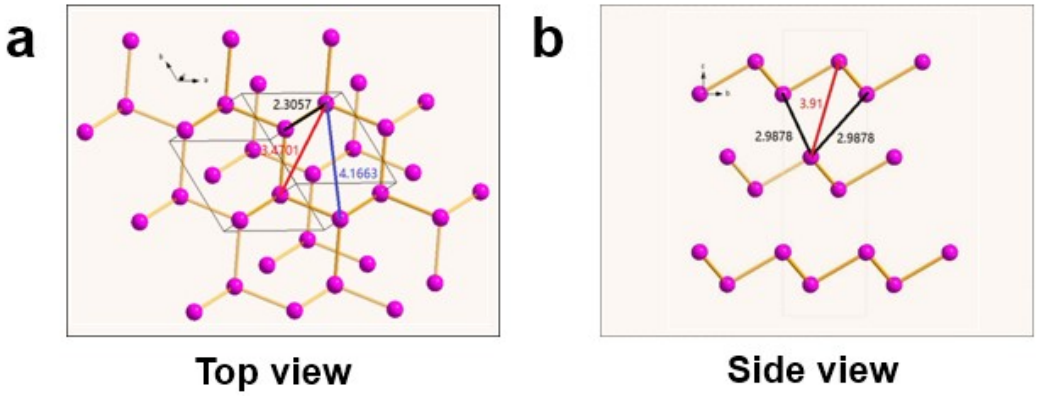

Fig. S1. Schematic diagram of R-3m GeP_5 from top view (a) and side view (b).

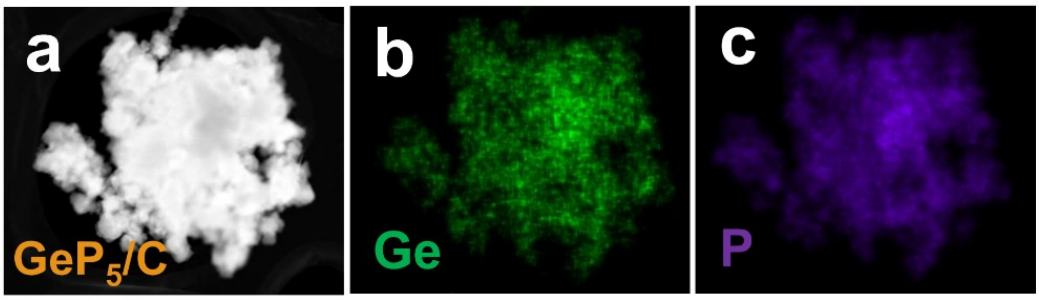

Fig. S2. The elemental mappings of GeP_5/C composite.

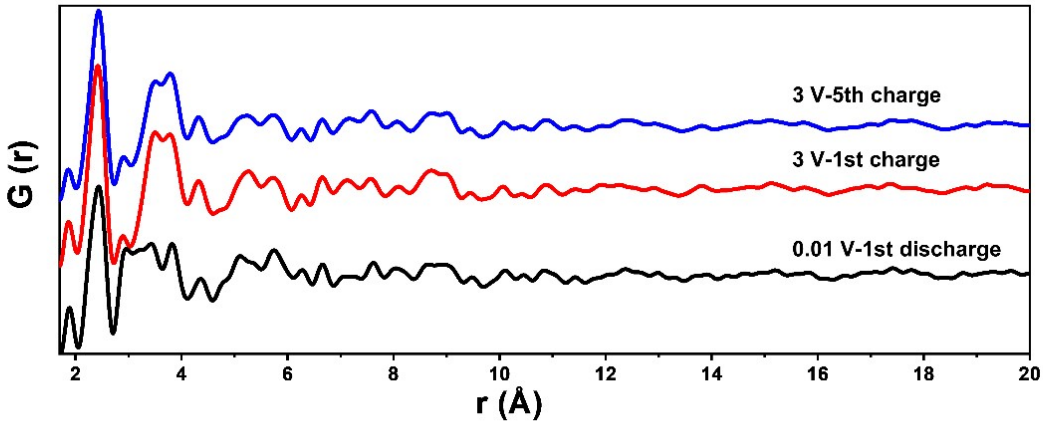

Fig. S3. Long-range PDF of GeP_5/C collected at the first discharged, first and fifth charged states within *r* range of 0-20 Å.

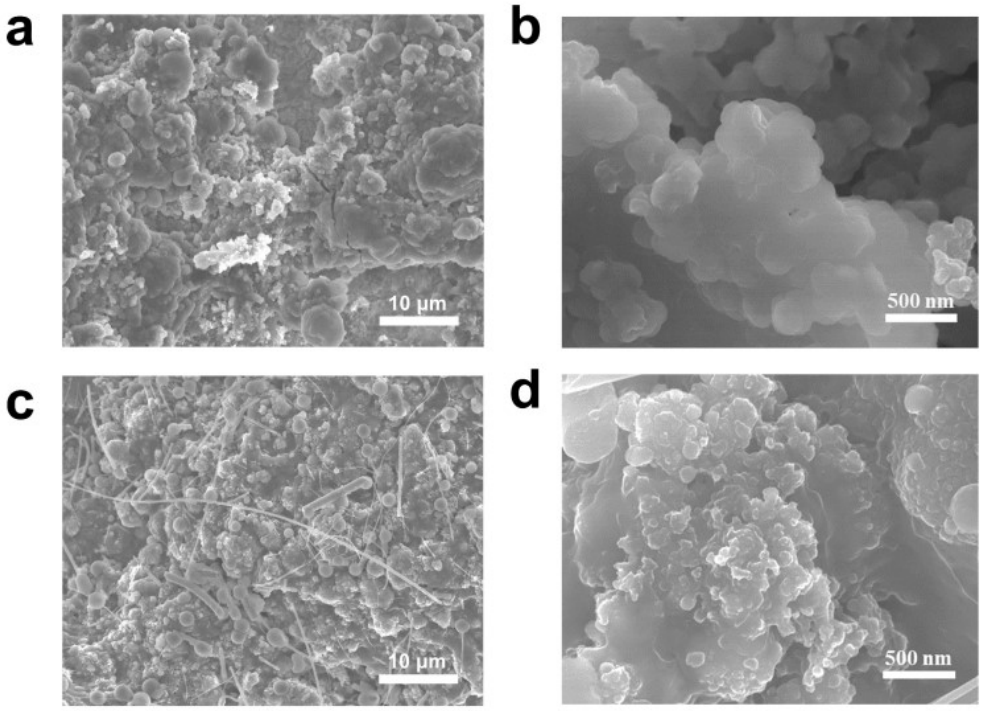

Fig. S4. SEM images of the GeP_5/C electrode at the fully discharged state (a, b) and fully charged state (c, d).