Supporting Information

In Situ TEM and Half Cell Investigation of Sodium Storage in

Hexagonal FeSe Nanoparticles

Kai Wu,^{#a} Fei Chen, ^{#a} Zhongtao Ma, ^{#a} Bingkun Guo,^a Yingchun Lyu,^a Peng Wang,^{ac} Hangsheng Yang,^d Qianqian Li,^{*a} Hongtao Wang,^{*c} and Anmin Nie,^{*ab}

^aMaterials Genome Institute, Shanghai University, Shanghai 200444, China

^bCenter for High Pressure Science, State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

^cCenter for X-mechanics, Zhejiang University, Hangzhou 310027, China

^dState Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

[#]These authors contributed equally to the work.

To whom correspondence should be addressed. E-mails: anmin@ysu.edu.cn (Anmin Nie), htw@zju.edu.cn (Hongtao Wang), and qianqianli@shu.edu.cn (Qianqian Li)

Supplementary experiment

In addition, we also synthesized the tetragonal FeSe (*t*-FeSe) sample. Fig. S6b shows the crystal structure of *t*-FeSe, and Fig. S7 shows the XRD (JCPDS card no. 85-0735 ESI⁺). Under the same experimental conditions, we found that, at the beginning, the discharge capacity of the *t*-FeSe is higher than the *h*-FeSe in Fig. S8a (ESI⁺). However, the better cycling performance of the *h*-FeSe is demonstrated after the 65th cycle with the stability performance of the *h*-FeSe electrode in sodium-ion batteries. At the same time, by comparing electrochemical impedance spectra of *h*-FeSe and *t*-FeSe electrode before testing, it shows smaller kinetics hindrance of charge-transfer reaction for the *t*-FeSe electrode in Fig. S8b, illustrating that the irreversible phase transformation in the first circle can reduce the resistance of the electrode.

Considering the different conditions between nanobattery and actual battery testing, we have added more experiments here to further prove the conclusion in the manuscript.

The XPS spectra obtained from the electrode samples after discharge are shown in Fig. S9 (ESI⁺). According to the previous reports ¹⁻², the spectra of the peak at 1072.2 eV are ascribed to Na 1S, and two main peaks at 54.6 and 55.8 eV relate to the binding energy of Se 3d. In Fig. S9c, the peaks at 708.8 and 721.9 eV are characteristic for Fe⁰ 2p, the peaks at 710.6 and 723.8 eV correspond to Fe²⁺ 2p, and the peaks at 712.7 and 725.8eV correspond to Fe³⁺ 2p. Although these components of the electrode are susceptible to the oxygen and moisture in air after full sodiation, it can still be conformed that Na₂Se and Fe are existed in the final phases based on the results above.

The electrode material after charge has also been characterized by *ex situ* XRD, as shown in Fig. S10 (ESI⁺). After the first cycle, the peaks of *h*-FeSe disappear, and the new peaks occur at 28.53°, 47.30°, which are attributed to *t*-FeSe, further validating the results of the SAED pattern.

Fig. S11 (ESI⁺) shows TEM image, SEAD pattern and HRTEM image of the electrode after 5 charge cycles. The diffraction rings can be indexed by polycrystalline *t*-FeSe phase. The HRTEM image displays one *t*-FeSe nanoparticle has single crystal structure with size of ~5 nm, the d-spacing of ~0.307 nm corresponds to the {101} plane of *t*-FeSe phase. It is worth noting that both amorphous and polycrystalline *t*-FeSe are co-existed in the final products. The HRTEM image of the electrode further validates the results of the SAED pattern and provides new evidence for the electrochemical reaction processes in sodium-ion battery.

After the first desodiation, the new phase of *t*-FeSe phases are formed based on *in situ* TEM and *ex situ* XRD results. The formation of the layered tetragonal phase structure makes the insertion of sodium ions easier. As shown in Fig S3., after the 1st cycle, the cathodic peaks of 1.71 V, 1.29 V correspond to the insertion of sodium ions and the formation of Na_xFeSe, and the peak of 0.78 V corresponds to the conversion reaction forming Na₂Se and Fe³⁻⁵. During the anodic scan, the oxidation peaks of 1.53 V, 1.97 V correspond to the extraction of sodium ions and the formation of *t*-FeSe, which is same as the charge process in the first cycle. Na₂Se and Fe formed in the sodiation process will firstly transform into Na_xFeSe with a stable layered tetragonal structure (I4/mmm)⁶⁻⁸. Considering the minimum energy path of intercalated Na ions, the interlayer distance of Na_xFeSe will gradually decrease due to the extraction of Na ions. At the end of the desodiation process, the formation of the layered *t*-FeSe has the lowest energy and the most possibility when all of the Na ions are released from the crystal lattice. The discharge and charge total reaction process of *h*-FeSe can be summarized as below.

The discharge reaction after 1st cycle:

t-FeSe + 2Na ⁺ + 2e ⁻ → Na ₂ Se + Fe	(3)
The discharge reaction:	
$Na_2Se + Fe \rightarrow t$ -FeSe + 2Na ⁺ + 2e ⁻	(4)

Synthesis of Materials

Fe and Se powders were uniformly mixed together with different element molar ratio of 1: 1.02 and 1.02: 1 for *h*-FeSe and *t*-FeSe, respectively. Then the mixture was sealed into an evacuated quartz tube and heated up to 700 °C for 24 h. After cooling to room temperature, bulk materials were picked out and ground to powders in the agate mortar for 60 min. Next, the powders were dispersed and exfoliated in N-Methyl pyrrolidone (NMP) with concentration of 1 g L⁻¹ by ultrasonic processor for 3 h in ice-bath. The purpose of NMP solvent is to prevent the sample oxidation, and the ice bath is used to maintain the exfoliation temperature. As shown in Fig. S1, the size of the particles was effectively thinned down and the particle sizes are mainly in the range between 30 and 150 nm after ultrasonic treatment. Refinement of particle size can effectively improve performance in the subsequent electrochemical tests. The dispersion was centrifuged at 5000 rpm for 30 min and then dried at vacuum oven.

Characterization

The structure and phases information of the *h*-FeSe nanoparticles were identified by Xray diffraction (XRD, Bruker-D2, Germany) with Cu K α radiation (λ = 1.5418 Å) in the 20 range of 10° to 90°. The Rietveld refinement was achieved by software GSAS to analyse the *h*-FeSe purity^{9,10}. The X-ray photoelectron spectra (XPS) were obtained to investigate the samples with an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Scientific, America). The morphologies and components of the products were characterized by fieldemission scanning electron microscopy (FESEM, Zeiss Merlin, Germany) at an acceleration voltage of 5 kV, equipped with an energy-dispersive spectroscopy (EDS). The detailed structure of nanoparticles was characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM, JEM-2100, JEOL, Japan) with an accelerating voltage of 200 kV.

In situ TEM testing

The nanobattery setup was built on the X-Nano TEM holder, which was developed at the Center for X-Mechanics, Zhejiang University. It consists a compact four-degree freedom (positioning in X, Y, Z-directions plus self-rotation) nano-manipulator and in-situ electrical biasing function. The nanobattery system was designed in previous reports¹¹⁻¹³. The *h*-FeSe nanoparticles were pasted on one end of the Au rod as the working electrode. Sodium metal was coated on the tungsten probe as the counter electrode in the sodium-ion batteries. Na₂O and NaOH formed on the surface of sodium metal surface acted as solid electrolytes in the nanobattery system. The counter electrode was controlled to contact with the *h*-FeSe nanoparticles with a moving resolution of 1 nm. Then, in order to stimulate the sodiation / desodiation reaction, a negative/positive bias was applied between the two electrodes. The real-time *in situ* TEM images and electron diffraction patterns were involved to reveal the morphology evolution and phase transition of *h*-FeSe in electrochemical cycles.

Electrochemical Measurements

The working electrode materials consisted of 80 wt% of *h*-FeSe, 10 wt% of ketjen black carbon and 10 wt% of carboxy methyl cellulose (CMC) binder. The powders were dissolved into deionized water, stirred for 60 minutes at room temperature. Then the slurry was pasted on a clean copper foil. The resulting foil was punched into discs with diameter of 100

mm with average mass loading of ~1.5 - 2.0 mg cm⁻² in each electrode. Electrochemical tests were carried out in 2032-coin cells, assembled in an Ar-filled glove box using the asprepared electrode as a working electrode, a sodium metal disk as the counter and reference electrode, glass fibre as the separator, 1.0 mol L⁻¹ sodium trifluoromethanesulfonate (NaCF₃SO₃) dissolved in the solvent of diethylene glycol dimethyl ether (DEGDME) as electrolyte. Galvanostatic charge-discharge curves, cycling performances and rate capabilities were performed between 0.1 and 2.5 V (*vs.* Na/Na⁺) on CT2001A LAND test system. Cyclic voltammograms (CV) was conducted using coin cells on an electrochemical workstation (Celltest 1470E, Solartron Analytical, UK) in the voltage range of 0 - 3.0 V (*vs.* Na/Na⁺) at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectra (EIS) were measured on an electrochemical workstation (Celltest 1400, Solartron Analytical, UK) over a frequency range of 0.1 Hz - 100 kHz with an amplitude of 10 mV. All of the electrochemical tests were carried out at 25 °C.

References

- 1. K. Zhang, T. Zhang, J. Liang, Y. Zhu, N. Lina, and Y. Qian, RSC Adv., 2015, 5, 14828-14831
- 2. M. A. Muñoz-Márquez, M. Zarrabeitia, E. Castillo-Martínez, A. Eguía-Barrio, T. Rojo and M. Casas-Cabanas, *ACS Appl Mater Interfaces*, 2015, **7**, 7801-7808.
- 3. X. Wang, Z. Yang, C. Wang, L. Ma, C. Zhao, J. T. Chen, X. Zhang and M. Xue, *Nanoscale*, 2017, **10**, 800.
- 4. A. Zhang, T. Xia, L. Kai, T. Wei, Z. Yang and Q. Zhang, Sci Rep, 2013, 3, 1216.
- 5. W. Min, Z. Rui, K. Chen, G. Liu, W. Chen, L. Wang, Z. Nan, L. Xue, W. Zhang and Y. Huang, *Energy Storage Materials*, 2018, **10**, 114-121.
- 6. Z. Jiang, G. Xiao, L. Wang and H. Li, Chem. Phys. Lett., 2016, 659, 230-233.
- 7. G. D. Park, J. H. Kim and C. K. Yun, *Materials Characterization*, 2016, **120**, 349-356.
- 8. T. Kajita, T. Kawamata, T. Noji, T. Hatakeda, M. Kato, Y. Koike and T. Itoh, *Physica C*, 2015, **519**, 104-107.
- 9. B. H. Toby, J. Appl. Crystallogr., 2001, **34**, 210-213.
- 10. B. H. Toby and R. B. Von Dreele, J. Appl. Crystallogr., 2013, 46, 544-549.
- 11. H. Asayesh-Ardakani, W. Yao, Y. Yuan, A. Nie, K. Amine, J. Lu and R. Shahbazian-Yassar, *Small Methods*, 2017, **1**, 1700202.
- 12. Q. Li, J. Wu, J. Xu and V. P. Dravid, J. Mater. Chem. A, 2016, 4, 8669-8675.
- 13. A. Nie, Y. Cheng, S. Ning, T. Foroozan, P. Yasaei, W. Li, B. Song, Y. Yuan, L. Chen and A. Salehikhojin, *Nano Lett.*, 2016, **16**, 2240-2247.



Fig. S1. SEM images of *h*-FeSe sample (a) before and (b) after ultrasonic treatment with the corresponding particle size distribution (The particle sizes are mainly in the range between 30 and 150 nm).



Fig. S2. The energy-dispersive X-ray (EDX) of *h*-FeSe nanoparticles. (a) SEM image and the corresponding EDX elemental mapping images for (b) Fe and (c) Se (the atomic ratio of the elements is 1: 1).



Fig. S3. Cyclic voltammetry for the first five cycles in a voltage window of 0 - 3.0 V at a scanning rate of 0.1 mV s⁻¹.



Fig. S4. Electrochemical impedance spectra (EIS) of the h-FeSe nanoparticles electrodes in the frequency range between 0.1 Hz - 100 kHz.



Fig. S5. (a-b) In situ TEM images of the *h*-FeSe nanoparticle far from sodium during the first sodiation and desodiation. (c-d) Plot of the reaction area varied with time, corresponding to the (a) and (b), respectively.



Fig. S6. (a) The crystal structure of *h*-FeSe. (b) The crystal structure of *t*-FeSe with the layer structure held through Van der Waals forces.



Fig. S7. XRD patterns of *t*-FeSe materials (JCPDS card no. 85-0735).



Fig. S8. (a) Discharge Capacity of the *h*-FeSe and *t*-FeSe electrodes in a voltage window of 0.1 - 2.5 V at a current density of 0.5 C. (b) Electrochemical impedance spectra (EIS) of the *h*-FeSe and *t*-FeSe electrodes before testing in the frequency range between 0.1 Hz - 100 kHz.



Fig. S9. XPS for the electrode after discharge at 5th cycle with Na_2Se and Fe. (a) Na 1S, (b) Se 3d, (c) Fe 2P.



Fig. S10. XRD pattern evolution of the electrode material from h-FeSe to t-FeSe after the first discharge/charge cycle in a voltage window of 0.1 - 2.5 V at a current density of 0.5 C.



Fig. S11. (a) TEM image with the corresponding SEAD pattern and (b) HRTEM image of the electrode with *t*-FeSe phase after charge 5 cycles.

Movie S1. In situ TEM observation of the *h*-FeSe nanoparticle morphology changes during the first sodiation.

Movie S2. In situ TEM observation of the *h*-FeSe nanoparticle morphology changes during the first desodiation.