Supplementary Info

Na₂Fe₂Se₂O. A Double Anti-perovskite with Prevalence of Anionic Redox Activity in Na-ion Batteries.

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All preparations for syntheses, primary physical characterisation and electrochemical measurements including the cell assembly for *operando* experiments were done in an Ar-filled glovebox (MBraun, Germany) with concentrations of H_2O and $O_2 \le 1.0$ ppm.

Na₂Fe₂Se₂O was synthesised by a two-step solid-state route. In the first step, stoichiometric amounts of Na (Alfa Aesar, 99.9%), FeO (Thermo Fisher Scientific, 99.5%), FeSe (synthesized) and Se (Thermo Fisher Scientific, 99.5%) were mixed (sodium lump was put on top of the powder mixture) and put into an alumina crucible. The total mass of reagents was equal to 0.5 g. The crucible was subsequently put into a quartz tube, which was evacuated to $5 \cdot 10^{-5}$ mbar and refilled with Ar up to 0.4 bar before melt sealing. After the preparation, the quartz ampoule was heated up to 773 K within 100 hours and kept at that temperature for 20 h using a muffle furnace. Afterwards, it was cooled down by shutting off the furnace. Before the second step of annealing, the powder was thoroughly reground and pressed into a pellet. The first annealing step was repeated, but temperature was increased to 873 K.

The synthesis of iron selenide was done initially from elemental Fe (Alfa Aesar, 99.5%) and Se powders by annealing the mixture in a quartz ampoule at 1023 K. The synthetic routines for FeSe and Na₂Fe₂Se₂O were adapted from the Ref. 8 of the main text.

Powder X-ray diffraction experiments were done on a STOE Stadi P diffractometer (Germany) equipped with a MYTHEN (Dectris) detector and curved germanium (111) monochromator, using CoKα₁ radiation.

Elemental composition of as-prepared samples was determined by iCAP 6500 Duo View (Fa. Thermo Fisher Scientific GmbH). Single element standards of 1 g/l concentration were used for calibration. Iron standard was self-prepared, basing on pure metal, Se standard was purchased from Alfa Aesar, and Na – from Thermo Fisher Scientific. Oxygen content was calculated from the difference between 100% and concentrations of other elements.

Table S1. Atomic parameters of structural refinement by the Rietveld method for the Na₂Fe₂Se₂O sample and the results of ICP-OES analysis. The site occupations were set to 100%. Space group *I4/mmm*, a = 4.1141(12) Å, c = 14.6684(6) Å.

Atom	Wyckoff site	X _f	Уf	Zf	U _{iso}
Na	4e	0	0	0.32715(9)	0.0464(4)
Fe	4c	0	0.5	0	0.0511(15)
Se	4e	0	0	0.12404(3)	0.0504(14)
0	2b	0	0	0.5	0.0630(9)

Element	Mass. %	Chemical formula	
Na	13.7(2)		
Fe	33.1(5)		
Se	47.2(8)	Na _{1.96(3)} Fe _{1.97(3)} Se _{1.98(3)} U _{1.14(9)}	
0	Found from the difference.		

The electrode composites represented a mixture of $Na_2Fe_2Se_2O$, conductive additive (Super P carbon black, Thermo Fisher Scientific, 99 %+) and polytetrafluoroethylene (Sigma Aldrich) binder in a mass ratio of 8:1:1. The mixture was pressed onto Al mesh, applying 2 t/cm² pressure. Swagelok[®] type electrochemical cells were used consisting of the working electrode and a counter electrode made of metallic sodium, separated by a glass fibre (Whatman, GF/D) soaked in 1 M NaPF₆/EC:DEC 1:1 v. electrolyte. Electrolyte preparation was done at 298 K.

Electrochemical measurements were done on a thermostated potentiostat (Biologic Instruments, France) at 253, 283, 298 and 313 K. The material was tested at least three times at each temperature by subsequently applying the current densities of 0.1 C, 0.2 C, 0.5 C, 1 C and 0.1 C at the end. 1 C corresponds to removal or extraction of 1 Na⁺ ion from a formula unit within an hour. Each sequence was repeated for 5 times, excluding the formation cycle. Note that at 313 K, instead of setting a constant lower potential cut-off, the amount of electric charge flowing through the electrochemical cell was controlled, to prevent the fast and irreversible degradation of the material at low voltages.

Instead of commonly used low rate cyclic voltammetry, where current is recorded as the response to voltage change, we used the differential capacity plots to evaluate the chemical diffusion coefficient of Na⁺ ion in the solid matter. The transition to the current *I* vs sq. root of dE/dt dependence from the dQ/dE function is as follows: dQ/dE has a dimension of mAh/V. Since we know the value of current

I from the galvanostatic experiment, we can divide the value of dQ/dE at the point of interest (shown in Fig. S2, panels d – f) by it, and take the reciprocal of the result to get the units of voltage change per time. Later on, the applicability of Randles-Sevcik equation is checked by plotting the current *I* vs sq. root of dE/dt. In panels g – j of the Figure S2, the linearity of this dependence is demonstrated for the selected peaks. Note, that differential capacity plots were built using the 3rd cycle at each current density, to characterize the stabilized system.

A peculiar point mentioned in the text is the coulombic efficiency at the first charge-discharge cycle of $Na_2Fe_2Se_2O$ -based cells. Panel k of Fig. S2 shows the corresponding differential capacity plot. The structure of $Na_xFe_2Se_2O$ seems to uptake significantly more Na^+ ions than the initially extracted amount. This feature of the system may be an argument for the partial decomposition of $Na_2Fe_2Se_2O$, and



Figure S2. a - c - typical galvanostatic charge-discharge curves for Na₂Fe₂Se₂O at elevated and reduced temperatures, <math>d - f - corresponding differential capacity plots, g - j - linearity of current and sq. root of voltage change rate relation for the Randles-Sevcik equation, k - differential capacity plot for the formation cycle of Na₂Fe₂Se₂O at room temperature, I - rate capability tests at four different temperatures.

becomes even more visible at elevated temperatures, and significantly less at lower temperatures.

Operando X-ray absorption and X-ray diffraction experiments were conducted using specific dedicated coin cells with Kapton (for XAS) or glass (for XRD) windows. 8-fold coin cell holder designed for *operando* measurements²⁸ connected to a potentiostat (Biologic, France) was used to collect the electrochemical data.

X-ray absorption spectra were recorded in both transmission and fluorescence yield modes at the beamline P64 of DESY (Hamburg, Germany)¹⁶. In the first case, ionisation chambers filled with appropriate mixture of inert gases served as detectors, in the latter PIPS detector was applied.

X-ray diffraction was done using the same electrochemical set-up at the beamline P02.1 of DESY (Hamburg, Germany¹⁵. Data acquisition was done by a Perkin Elmer XRD1621 CN3 - EHS (200×200 μm² pixel size, 2048 x 2048 pixels area) detector.

Figure S3 is showing the supplementary data for the information from *operando* studies presented in the main text. For XAFS analysis, the following routine was applied. First, the data were normalized and the background was subtracted. Then, transformation to the k-space (k is a wave number) was done. Afterwards, the data were "weighted", meaning multiplying by k³, to make the desired oscillations more visible. In the end, Fourier transformation of the obtained function $k^3 \cdot \chi(k)$ was done, in order to get the dependence $\chi(R)$, where R corresponds to the radial distance from the scattering atom. The distances in the first and second coordination spheres were evaluated using the least-square fitting method implemented as FEFF-code into Demeter software. For the fitting, corresponding crystallographic models were used.



Figure S3. Operando X-ray absorption spectroscopy of a – Fe K-edge and b – Se K-edge during discharge of $Na_2Fe_2Se_2O$, c- relative shifts of Fe and Se K-edges from their initial positions on the energy grid, d – the distances in the first coordination sphere of Se calculated from the XAFS function; and additional data for operando XRD: e – evolution of the cell volume of $Na_xFe_2Se_2O$ during the cell cycling, f – change of the selected Bragg reflections between pristine, charged and discharged states.

Additional reference for the SI:

28. M. Herklotz, J. Weiß, E. Ahrens, et al., J. Appl. Cryst., 2016, 49, 340.