

Structure Determination and Reaction Mechanisms of an Earth Abundant Sodium Battery Electrode

Sodium-ion batteries are becoming increasingly important due to the rapidly growing demand for electric energy storage technology. A new positive electrode material, sodium iron sulfate $\text{Na}_{2+2x}\text{Fe}_{2-x}(\text{SO}_4)_3$, has been developed, using only abundant elements in the Earth's crust. The compound shows a high working voltage of 3.8 V vs. Na/Na^+ with good high-rate capability. High-resolution powder diffraction revealed the crystal structure of the $\text{Na}_{2+2x}\text{Fe}_{2-x}(\text{SO}_4)_3$ through an *ab initio* structure determination procedure. This structure has two kinds of large one-dimensional tunnels, which are suitable for sodium ion transport. *In operando* diffraction of an $\text{Na}_{2+2x}\text{Fe}_{2-x}(\text{SO}_4)_3/\text{Na}$ electrochemical cell clearly demonstrated continuous and smooth lattice volume change without any transitions during charge-discharge processes.

Technology for storing energy, especially electrical energy, is crucial to realize a greener society. The lithium-ion battery (LIB) caused a paradigm shift in the mobile storage of electrical energy owing to its high voltage and high energy density. Its applications are now growing from small and mobile devices toward larger-scale systems. In view of this trend, the sodium-ion battery (SIB) is a candidate for practical energy storage systems [1]. An intrinsic problem that has hindered the commercialization of the SIB is its lower voltage due to higher electrodeposition potential of Na/Na^+ than Li/Li^+ by ca. 0.3 V. This limits the potential of the negative electrode, and hence the cell voltage becomes lower. To overcome this issue, it is necessary to develop a positive electrode with a higher potential.

A new electrode material, $\text{Na}_{2+2x}\text{Fe}_{2-x}(\text{SO}_4)_3$ (NFS), has been found by exploring the binary sulfate $\text{Na}_2\text{SO}_4\text{-FeSO}_4$ system, which consists only of the abundant elements Na, Fe, S and O. Sulfate (sulfuric acid) is one of the most produced engineering chemicals. Electrochemical tests of NFS/Na cells show a high working voltage of 3.8 V vs. Na/Na^+ , which is comparable with that of commercial LIBs. This corresponds to the highest $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential ever reported. Furthermore, the NFS electrode shows high-rate capability: reversible capacity exceeds 50% of the full capacity even at 3 minutes of charging/discharging.

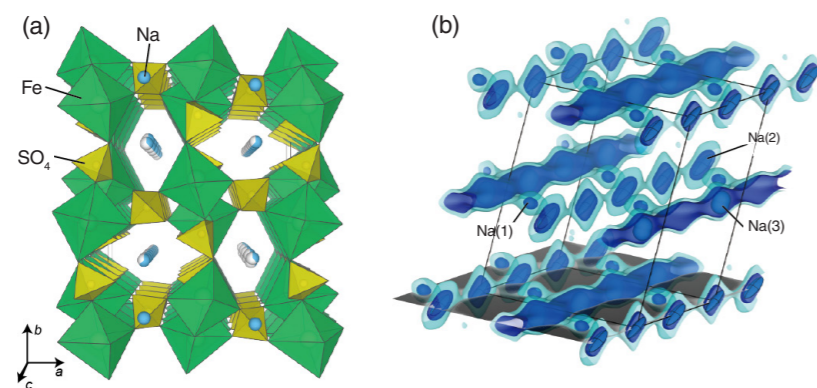


Figure 1: (a) Crystal structure of $\text{Na}_{2+2x}\text{Fe}_{2-x}(\text{SO}_4)_3$. (b) Bond-valence mismatch (ΔV) mapping. Blue and cyan equivalent surfaces represent 0.25 and 0.5, respectively.

The crystal structure of the NFS was determined by powder X-ray diffraction (XRD) at BL-4B2. High-resolution diffraction patterns were collected by a multi-detector system in which Ge(111) analyzers were installed for each detector to ensure sufficiently high angular resolution. The high-resolution data facilitates indexing and initial phase reconstruction from complex diffraction patterns for *ab initio* structure solution. The observed reflections were indexed by a C-centered monoclinic lattice and the initial structure was derived by the charge-flipping method. Figure 1(a) illustrates the crystal structure model of the NFS after subsequent Rietveld refinements. The structure is essentially isostructural to alluaudite, which is a kind of phosphate mineral [2]. Fe is surrounded by $[\text{SO}_4]^{2-}$ anions in a distorted octahedral geometry and forms a three-dimensional framework structure, where two kinds of large tunnels run parallel with the c-axis. The Na ions occupy three crystallographic positions: Na(1), Na(2) and Na(3). The Na(2) and Na(3) are in the two large tunnels, respectively. Spatial bond valence analysis revealed that the accessible space for Na is spread along the tunnel [3]. These structural features should contribute to high Na ionic conductivity.

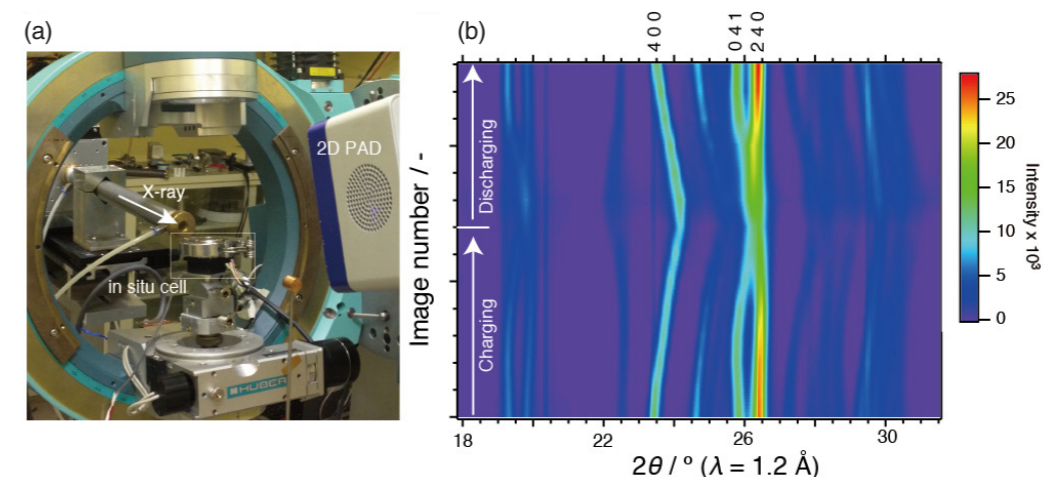


Figure 2: (a) Experiment setup for *in operando* XRD at BL-3A. (b) Two-dimensional representation of time series of *in operando* XRD patterns.

Changes in the crystal structure during the battery reaction were traced by *in operando* X-ray diffraction at BL-3A. The cell was set in a pseudo symmetric reflection geometry [Fig. 2(a)]. The scattered X-ray was detected by a two-dimensional pixel array detector (2D-PAD: PILATUS 100K, DECTRIS) within shutter-less exposure. Figure 2(b) shows a time series of the *in operando* XRD patterns, where the cell was operated in a galvanostatic (constant current) mode with 0.2 C rate (5 hours for charging and discharging, respectively). Each pattern was collected in an exposure time of 10 seconds. All the reflections show continuous shift during the operation. No additional reflections appeared. These results confirm that neither phase separations nor first-order phase transitions occur during the battery operation. This feature may contribute to stable cycling of the battery, since such drastic transitions frequently cause significant degradation of the electrode.

Synchrotron experiments at the Photon Factory provided critical information about the structure of the com-

pletely new electrode material [4]. These important findings will contribute to further improvement of the battery performance through further exploration and design of new materials with higher reaction voltage, faster ionic-electronic transport, larger reversible capacity, and so forth.

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BEAMLINES

BL-3A and BL-4B2

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