

Sodium Transport Mechanism in an Earth-Abundant Cathode Material for Sodium-Ion Batteries

Lithium- and sodium-ion batteries are important energy storage technologies for mobile and stationary electric power sources. The rapid growth of the use of energy storage devices requires the design of new battery materials with abundant elements. A sodium iron sulfate with alluaudite structure, $\text{Na}_{2.5}\text{Fe}_{1.75}(\text{SO}_4)_3$ (NFS), was recently developed as a positive-electrode active material for sodium-ion batteries [1]. This material is composed only of abundant elements and exhibits superior performance with high redox potential and good rate capability. To understand the origin of the novel performance of NFS, a combined analysis of X-ray and neutron diffraction was used to analyze the crystal structure and sodium disordering, coupled with the dynamics of sodium transport. The sodium density distribution determined by the diffraction analysis revealed a characteristic one-dimensional channel suitable for sodium transport [2].

Energy storage technology is a key for making society greener. Lithium- and sodium-ion batteries are the main types of electric energy storage used as power sources for mobile electronics and electric/hybrid vehicles. Since the demand for these batteries is rapidly growing for broader applications, new battery materials using abundant elements need to be developed for the sustainability of society. The sodium-ion battery is the most promising candidate for sustainable battery systems, as its constituent materials are all widely available [3].

Recently we developed a new material, alluaudite-type sodium iron sulfate $\text{Na}_{2+2x}\text{Fe}_{2-x}(\text{SO}_4)_3$ ($x \sim 0.25$), (NFS) for the positive electrode of sodium-ion batteries [1, 4]. This material is composed only of the earth-abundant elements Na, Fe, S and O, and exhibits high redox potential and high-rate capability. Accordingly, NFS is highly promising as a positive electrode material for sodium-ion batteries. For the further development of electrode materials, it is necessary to understand

the fundamental properties and mechanisms related to electrochemical reactions in the battery. The rate capability of an electrode active material is controlled by the ionic transport properties of the material. Thus, understanding the ionic conduction mechanism is vital when designing the material of the battery electrodes.

The ionic conductivity in a crystalline material is closely related to the crystal structure and local environment of mobile species. Thus, a detailed analysis of the crystal structure will provide a clear insight to understand the ionic conduction properties. The crystal structure of NFS was determined by high-resolution powder X-ray diffraction at BL-4B2 [1, 4]. Figure 1 shows a typical powder X-ray diffraction pattern of NFS measured by the multiple detector system at BL-4B2. NFS crystallizes in a monoclinic lattice with three-dimensional framework structure composed of Fe(II) and tetrahedral sulfate anions. The Na ions sit at three kinds of interstitial sites of the iron sulfate framework. Two of the Na sites, Na2 and Na3, form one-dimensional tunnel structures.

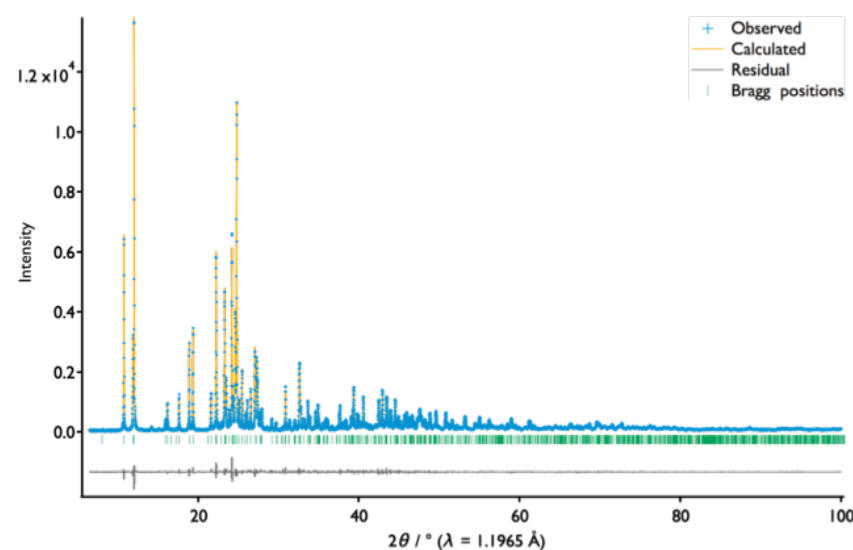


Figure 1: Observed and calculated high-resolution X-ray diffraction patterns of NFS.

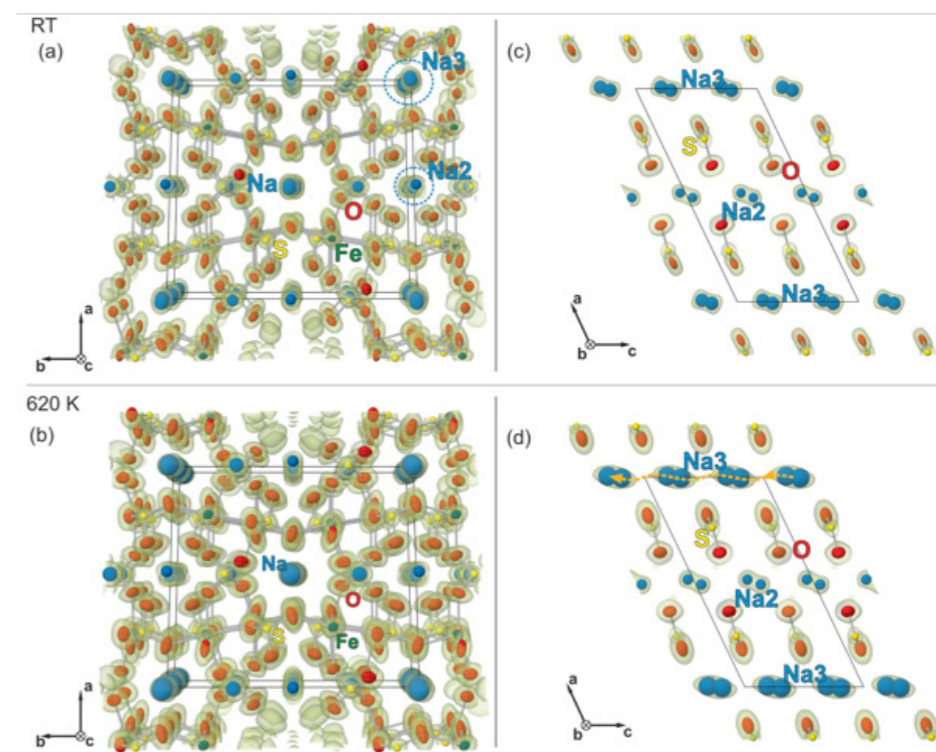


Figure 2: Crystal structure and isosurface of nuclear density of NFS derived from high-temperature powder diffraction data.

To unveil the detailed sodium-transport mechanism in NFS, a combined analysis of X-ray and neutron powder diffraction was conducted. High-temperature *in situ* measurements were performed at BL02B2 of SPring-8 and BL08 of J-PARC MLF, and analyzed by the Rietveld method. Subsequently the derived structure factors were processed by the maximum entropy method (MEM) to reconstruct the nuclear density distribution. A computer program, Dysnomia, was used for the MEM [5]. High-resolution powder diffraction data revealed a significant positional disordering of Na even at room temperature. At a higher temperature, just below the decomposition temperature of NFS (620 K), thermal motion of the constituent ions was clearly activated, as shown in Fig. 2. The mobile Na ions showed characteristic anisotropy of nuclear density distributions. Especially, Na3 showed an anomalous spreading of density distribution along the [001] direction. Compared to Na3, the other Na sites, Na1 and Na2, showed limited temperature dependence. These features suggest that the tunnels running on the Na3 sites are much more suitable for Na ion transport than the other pathways, and may dominate the ionic conductivity in NFS.

In summary, alluaudite NFS has a large tunnel-like pathway suitable for Na transport. The structure along the Na3 sites is crucial to maximize the ionic conductivity of alluaudite-type compounds. Other Na sites could be activated further by optimizing other pathways collateral to the Na3 channel.

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