Sodium intercalation in the phosphosulfate cathode NaFe$_2$(PO$_4$)(SO$_4$)$_2$

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HIGHLIGHTS

- NaFe$_2$(PO$_4$)(SO$_4$)$_2$ was prepared for the first time as pure phase.
- Its crystal structure was solved using the combination of powder XRD and HRTEM.
- NaFe$_2$(PO$_4$)(SO$_4$)$_2$ is a 3 V cathode for sodium ion batteries.
- The ionic diffusivity and electrical conductivity measurements were carried out.
- The interfacial kinetics as a function of sodium concentration were studied.

GRAPHICAL ABSTRACT
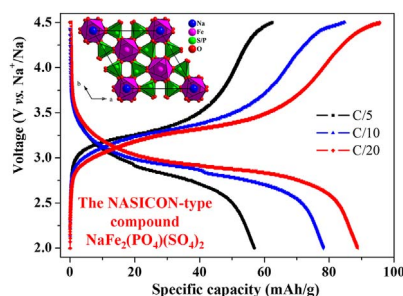
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ABSTRACT

The compound NaFe$_2$(PO$_4$)(SO$_4$)$_2$ is successfully synthesized via a solid state reaction route and its crystal structure is determined using powder X-ray diffraction data. NaFe$_2$(PO$_4$)(SO$_4$)$_2$ phase is also characterized by cyclic voltammetry, galvanostatic cycling and electrochemical impedance spectroscopy. NaFe$_2$(PO$_4$)(SO$_4$)$_2$ crystallizes with the well-known NASICON-type structure. SAED and HRTEM experiments confirm the structural model, and no ordering between the PO$_4^{-3}$ and SO$_4^{-2}$ polyanions is detected. The electrochemical tests indicate that NaFe$_2$(PO$_4$)(SO$_4$)$_2$ is a 3 V sodium intercalating cathode. The electrical conductivity is relatively low (2.2×10^{-6} Scm^{-1} at 200 °C) and the obtained activation energy is ~0.60eV. The GITT experiments indicate that the diffusivity values are in the range of 10^{-11}-10^{-12} cm^2/s within the measured sodium concentrations.

1. Introduction

Compounds of the NASICON (NAtrium Super Ionic CONductor) family are being reinvestigated as electrode materials for sodium-, lithium-, and magnesium-ion batteries [1–4]. Previously, they were extensively studied for their luminescence and gas sensor-properties [5–7], and as potential hosts for radioactive waste [8]. Of significance, NASICON compounds possess solid electrolytes properties owing to their pronounced ionic conductivity. Goodenoogh et al. first reported the high ionic conductivity of 0.2 S.cm^{-1} at 573 K for Na$_{1+x}$Zr$_2$Si$_x$P$_{3-x}$O$_{12}$ ($0 \leq x \leq 3$) [9].

The first NASICON compound NaZr$_2$(PO$_4$)$_3$, belonging to the family A$_x$M$_2$(XO$_4$)$_3$, was synthesized by Sljukic et al. in 1967 [10], and its crystal structure was solved a year later by Hagman and Kierkegaard [11]. The structure has the rhombohedral symmetry space group R-3c and consists of 3D M$_2$(XO$_4$)$_3$ skeleton made of corner sharing MO$_6$

octahedra and XO_4 tetrahedra. The high mobility of the "A" cations that are located in the interstitial sites often induces the formation of superstructures, leading to a rich $A_xM_2(XO_4)_3$ polymorph. Indeed, these compounds have been synthesized with a wide range of chemical compositions wherein "A" is either monovalent cations such as (Li^+, Na^+, K^+, Rb^+, NH_4^+, Cu^+, Ag^+), divalent cations such as (Sr^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}), trivalent cations such as (Al^{3+}, Ln^{3+} = rare earth), tetravalent cations such as (Ge^{4+}, Zr^{4+}, Hf^{4+}) or a vacancy. "M" can be either divalent, trivalent, tetravalent, or pentavalent cations such as (V^{5+}, Nb^{5+}, Ta^{5+}, Sb^{5+}, As^{5+}) [12] and refs. therein. "X" can be selected from Si, P, S, As, and Mo. The occupancy "x" for the "A" cation can range from 0 to 4. In addition to chemical composition abundance, the crystalline structure of NASICON had been portrayed apart from the main space group *R*-3*c* according to *R*-3, *R*3, *R*32, *P*-3c1, and *C*2/c in the cases of $NaSn_2(PO_4)_3$, $RbTi_2(PO_4)_3$, $Na_5Ti(PO_4)_3$, $La_{0.33}Zr_2(PO_4)_3$, and $Na_{3.20}Zr_{1.68}[PO_4]_{1.16}[SiO_4]_{1.84}$, respectively [13–17].

Previous works had shown that the compounds $Li_3Fe_2(PO_4)_3$ and $Fe_2(SO_4)_3$ exhibit rich crystal chemistries. $Li_3Fe_2(PO_4)_3$, which can be prepared by a solid state reaction, undergoes two reversible phase transitions: α ↔ β at 460 K and β ↔ γ at 523 K [18–20]. Both α- and β-phases are monoclinic (s.g. $P2_1/c$), whereas the γ-phase is orthorhombic (s.g. *Pbcn*). Another crystalline variety of $Li_3Fe_2(PO_4)_3$ belonging to the rhombohedral system (s.g. *R*-3) could also be prepared by ion exchange from γ-$Na_3Fe_2(PO_4)_3$ (s.g. *R*-3c) [21]. On the other hand, $Fe_2(SO_4)_3$, prepared by solid state reaction, undergoes only one reversible phase transition from monoclinic (s.g. $P2_1/c$) to rhombohedral (s.g. *R*-3) symmetry [22,23]. The insertion of lithium into the rhombohedral forms of $Li_3Fe_2(PO_4)_3$ and $Fe_2(SO_4)_3$ leads to Fe^{3+}/Fe^{2+} redox voltages operating at 2.8 and 3.6 V, respectively [24]. In the case of the mixed polyanionic NASICON $LiFe_2(SO_4)_2(PO_4)$, the voltage of the Fe^{3+}/Fe^{2+} redox couple, which is due to the insertion of lithium, is in the range of 3.3–3.4 V vs. Li^+/Li. The inductive effect of the XO_4 (X = P, S) groups, which weakens or strengthens the covalency of the Fe − O bond depending upon the electronegativity of X, is at the origin of these significant operating voltage differences [25]. Sodium compound counterparts have also been studied. Indeed, the $Na_3Fe_2(PO_4)_3$ phase undergoes two reversible phase transitions, α ↔ β at 368 K and β ↔ γ at 418 K, owing to the order/disorder rearrangements in the sodium sites within the [$Fe_2P_3O_{12}$] framework [26,27]. Less than one Na-atom can be inserted into $Na_3Fe_2[PO_4]_3$ and $Fe_2(SO_4)_3$ phases with the Fe^{3+}/Fe^{2+} redox couple activated at 2.5 and 3.0 V vs. Na^+/Na, respectively [28–30]. Recently, Barpanda et al. prepared a new sodium iron sulfate $Na_2Fe_2(SO_4)_3$ which crystallizes with the Alluaudite-type structure instead of NASICON [31], whereas Shiva et al. prepared the phosphosulfate $NaFe_2(PO_4)(SO_4)_2$ with large amount of impurities and a surprising electrochemical behavior such as capacity increase with cycling, which could not be interpreted by the authors [32].

In this paper, we report on the structural characterization, electrochemical performances and ionic and electronic transport properties of the pure NASICON-type $NaFe_2(PO_4)(SO_4)_2$ compound. The crystal structure was solved by the Rietveld method using powder X-ray diffraction (PXRD) data. SAED and HRTEM experiments confirmed the structural model. The electrochemical performances were examined by galvanostatic cycling and cyclic voltammetry. GITT and electrochemical impedance spectroscopy (EIS) were used to measure the ionic diffusivity, electronic conductivity, and interfacial charge transfer kinetics. The stability of the NASICON structure during cycling was also confirmed by *ex-situ* PXRD experiments.

2. Experimental section

2.1. Synthesis

$NaFe_2(PO_4)(SO_4)_2$ powder was synthesized via a solid state synthesis route from stoichiometric mixtures of $NaNO_3$ (Aldrich, ≥99%), Fe

$(NO_3)_3 \cdot 9H_2O$ (Merck, ≥99%), $(NH_4)_2SO_4$ (Aldrich, ≥99%), and $NH_4H_2PO_4$ (Aldrich, 99.99%). $NaNO_3$, $Fe(NO_3)_3 \cdot 9H_2O$, and $(NH_4)_2SO_4$ with a mole ratio of 1:2:2 were dissolved in 20 ml of water (Solution-A). $NH_4H_2PO_4$ was dissolved in 10 ml of H_2O (Solution-B). After stirring at room temperature for 10 min, solution-B was added to solution-A dropwise, and the new solution was stirred at 80 °C until evaporation of water. The obtained orange powder contained sodium nitrate and an amorphous phase. After calcination at 550 °C for 12 h under air a pure green powder of $NaFe_2(PO_4)(SO_4)_2$ was obtained. When carbon additives where added under argon several impurities appeared, therefore only the pure powder sintered in air was used for the electrochemical tests.

For electrical conductivity measurements, the $NaFe_2(PO_4)(SO_4)_2$ powder was sintered into pellets using the spark plasma sintering (SPS) technique at four different temperatures (400, 500, 600 and 700 °C). The pellets were heated for 1 min under a pressure of 30 MPa. Under the same conditions, the pellets were sandwiched with gold plates, which act as ionic blocking electrodes. Impurity free dense pellet was obtained at 600 °C. At 700 °C, the sample partially melted and decomposed, whereas at 400 and 500 °C, the pellets were not dense enough. Hence, the measurement was performed on the pellet sintered at 600 °C in order to exclude any erroneous results.

2.2. Elemental analysis

Semi-quantitative energy dispersive X-ray spectrometry (EDX) analyses were carried out with a SEM-Nova NanoSEM 450 scanning electron microscope. The experimentally observed Na/Fe/P/S atomic ratios were close to 1:2:1:2, as expected for $NaFe_2(PO_4)(SO_4)_2$.

2.3. Powder X-Ray diffraction measurements

To check the purity of $NaFe_2(PO_4)(SO_4)_2$, powder-XRD measurements were performed. The data were collected at room temperature over the 2θ − angular range of 12° ≤ 2θ ≤ 102° with a step size of 0.007° using a Panalytical diffractometer operating with the Cu-Kα radiation. The Rietveld refinement was performed using the Fullprof program package [33]. The background was estimated by a Legendre function, and the peak shapes were described by a pseudo-Voigt function. The refinement of peak asymmetry was performed using four Berar-Baldinozzi parameters. Evaluation of these data revealed the refined cell parameters listed in Table 1. The pellets that have been sintered at 400, 500, 600, and 700 °C were also analysed by PXRD measurements.

2.4. Electron diffraction investigations

Selected area electron diffraction (SAED) and high-resolution electron microscopy (HREM) were performed in a JEOL 3000 FEG electron microscope, fitted with a double tilting goniometer stage (± 22°, ± 22°). Local composition was analysed by energy-dispersive X-ray spectroscopy (EDS) with an Oxford INCA analyzer system attached to the above-mentioned microscope. Simulated HREM images were calculated by the multislice method using the MacTempas software package. The cationic composition, determined on several small crystallites by energy dispersive X-ray analysis in the electron microscope, is in agreement with the nominal one.

2.5. Thermal analysis

Thermal analyses (TG-DTA-MS) were carried out on the $NaFe_2(PO_4)(SO_4)_2$ sample using a Rigaku TG-DTA-PIMS410/s instrument. The measurements were conducted between 25 and 900 °C at a heating rate of 5 °C/min. The experiment was performed in alumina crucible under helium atmosphere. We clearly observe 30% of weight loss (Fig. S1). Based on the mass spectrometer analysis, this loss corresponds to two