Short communication

An *alluaudite* Na$_{2+2x}$Fe$_{2-x}$(SO$_4$)$_3$ $(x = 0.2)$ derivative phase as insertion host for lithium battery

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ABSTRACT

A new desodiated derivative compound, Na$_{0.89}$Fe$_{1.8}$(SO$_4$)$_3$, was prepared by the chemical oxidation of *alluaudite* Na$_{2.4}$Fe$_{1.8}$(SO$_4$)$_3$ phase using NOBF$_4$ as oxidant. The structure and valency of Fe were characterized by X-ray diffraction (XRD) and ^{57}Fe Mössbauer spectroscopy. Intercalation behavior of lithium ions in the structure of Na$_{0.89}$Fe$_{1.8}$(SO$_4$)$_3$ was gauged by electrochemical analyses and ex-situ X-ray diffraction. A high capacity of 110 mAh g^{-1} at 0.1 C was obtained with a good rate kinetics within a range of 0.1–10 C(1 C = 118 mAh g^{-1}) involving a high Fe^{3+}/Fe^{2+} redox potential of 3.75 V (vs. Li/Li$^+$). These results confirmed that the Na$_{2.4-\delta}$Fe$_{1.8}$(SO$_4$)$_3$ framework was stable even after oxidation and forms a new competitive cathode for the reversible intercalation of lithium ions.

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1. Introduction

Rechargeable batteries have attracted great attention due to their wide gamut of applications ranging from smart portable devices to (plug-in hybrid) electric vehicles. Designing robust batteries is a complex puzzle that takes into account not only electrochemical performance but also cost, safety and sustainability of materials and processes [1]. Cathode is a key component having significant influence on the final performance and cost of batteries. Realizing the next generation batteries rely on developing superior cathodes combining low cost and high energy-density that can be obtained by new materials with high theoretical capacity and/or high redox voltage. Ideal economic candidates will be Fe-based cathodes with high redox voltage: a goal that can be realized by many SO$_4$-based cathodes (fluorosulphates, orthosulphates etc.) [2–5] and pristine/modified pyrophosphate cathodes [6–9]. An alternate approach to design high-voltage cathode for Li-ion batteries is to use Na- and K-based analogues having large channels as host compound for efficient Li-insertion: e.g. KFeSO$_4$F can act as a host for lithiation forming isostructural LiFeSO$_4$F (3.7 V cathode) [10].

Recently, we have reported a new *alluaudite* framework, Na$_{2.4}$Fe$_{1.8}$(SO$_4$)$_3$, as cathode for Na-ion battery. A reversible capacity of 100 mAh g^{-1} was obtained along with the highest ever Fe^{3+}/Fe^{2+} redox potential located at 3.8 V (vs. Na/Na$^+$) [11,12]. Herein, using this

alluaudite framework, we have prepared its desodiated derivative Na$_{0.89}$Fe$_{1.8}$(SO$_4$)$_3$ via the chemical oxidation and investigated its electrochemical performance in lithium battery application for the first time. It delivers capacity exceeding 110 mAh g^{-1} with a high Fe^{3+}/Fe^{2+} redox potential situated at 3.75 V (vs. Li/Li$^+$), making it a novel economic Fe-based high-voltage insertion material for lithium batteries.

2. Experimental

Na$_2$SO$_4$ and FeSO$_4$ precursors with a molar ratio of 2:3 were ball milled for 6 h. The precursor mixture was calcined at 350 °C for 24 h in a tubular furnace with steady Ar flow giving rise to Na$_{2.4}$Fe$_{1.8}$(SO$_4$)$_3$. For chemical oxidation, 0.5 g of Na$_{2.4}$Fe$_{1.8}$(SO$_4$)$_3$ and 0.4736 g of NOBF$_4$ (molar ratio of 1:2) were dispersed into 40 ml acetonitrile and were stirred for 6–48 h. The resulting product was filtered, washed with acetonitrile several times and was dried at 60 °C for 6 h in vacuum oven. All materials' preparation/handling was conducted in an Ar-filled glove box to avoid any contact with moisture.

X-ray diffraction patterns were acquired with a Rigaku RINT-TTR III diffractometer equipped with a Cu-Kα source ($\lambda_1 = 1.5405$ Å) operating at 50 kV and 300 mA. For ex-situ XRD, the electrode was prepared using a mixture of active material and PTFE binder. At different intermittent states of (dis)charge, the electrode was recuperated and sealed inside an Ar-filled sample holder. The Mössbauer spectra were acquired with a Topologic System Inc. spectrometer with a ^{57}Co γ–ray source, calibrated with α-Fe as standard. The model fitting was performed with MossWinn 3.0 software.

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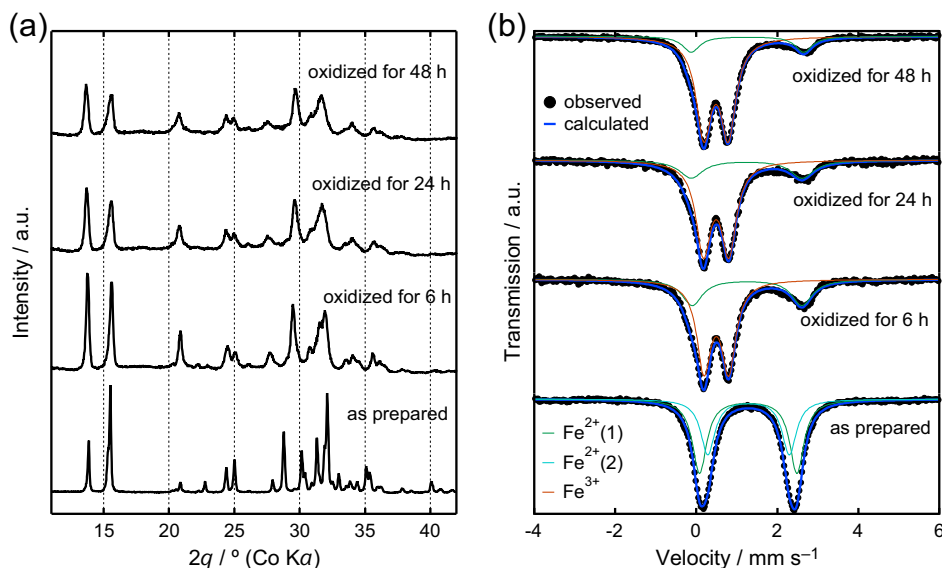*E-mail address:* yamada@chemsys.t.u-tokyo.ac.jp (A. Yamada).

Fig. 1. XRD patterns (a) and ^{57}Fe Mössbauer spectra (b) for the as prepared $Na_{2+2x}Fe_{2-x}(SO_4)_3$ and its oxidized compounds by $NOBF_4$ with various oxidation time.

For electrode formulation, the oxidized $Na_{0.89}Fe_{1.8}(SO_4)_3$, carbon black (Ketjen Black EC-600, LION corp.) and PVDF binder were mixed in a mass ratio of 8:1:1 in NMP solvent to form uniform slurry and were casted on an aluminum foil. The mass loading of $Na_{0.89}Fe_{1.8}(SO_4)_3$ was ~1.0 mg cm^{-2} with an estimated thickness of around 16 μm. Post drying in the vacuum oven, the foil was punched into circular discs with a diameter of 16 mm. 2032 type coin cell with the configuration of cathode|glass fiber separator|lithium metal was assembled inside the glove box, using 1.0 M LiPF$_6$ dissolved in ethylene carbonate/dimethyl carbonate (EC/DMC, v/v, 1/1) as electrolyte. Galvanostatic cycling was conducted in the voltage window of 2.0–4.8 V at different rates using TOSCAT-3100 unit. Cyclic voltammetry was conducted by the instrument of Biologic VMP3 within the voltage of 2–4.8 V under the scan rate of 0.1 mV s^{-1}.

3. Results and discussion

Fig. 1a shows the XRD patterns for the as prepared $Na_{2.4}Fe_{1.8}(SO_4)_3$ and its products of chemical oxidation. The as prepared phase has alluaudite-type structure with a monoclinic lattice in $C2/c$ symmetry. It consists of isolated edge-sharing Fe_2O_{10} dimers, which are in turn bridged together by SO_4 tetrahedral units strictly by corner-sharing mode, thereby forming a three-dimensional framework with large tunnels along c axis. Owing to chemical oxidation, which induce desodiation from the host framework:
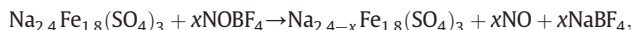
$$Na_{2.4}Fe_{1.8}(SO_4)_3 + xNOBF_4 \rightarrow Na_{2.4-x}Fe_{1.8}(SO_4)_3 + xNO + xNaBF_4,$$

the peak width and intensity become broader and weaker and the background scattering becomes stronger along with the depth of chemical oxidation. These changes indicate the occurrence of some structural disordering and lowering of crystallinity. Note that the chemical oxidation was very fast in the initial 6 h but slowed down with time, as confirmed by the Mössbauer spectroscopy (Fig. 1b). For example, the Fe^{3+} content increased from 0 to 69.8% in the first 6 h, but it increased slowly to the value of 76.0% in 24 h and to the maximum of 84.2% in 48 h. The initial fast reaction rate demonstrates easy extraction of sodium ions from the large channels running along the c-axis, in sync with the excellent rate capability of $Na_{2.4}Fe_{1.8}(SO_4)_3$ reported recently [11]. As discussed above, the maximum oxidation degree of 84.2% corresponds to $Na_{0.89}Fe_{1.8}(SO_4)_3$ as determined by the Mössbauer spectroscopy (Fig. 1b, Table 1). Besides, the isomer shift values in Mössbauer analysis are consistent with 1.27 mm s^{-1} of typical α-Fe^{II}SO$_4$ and 0.49 mm s^{-1} of monoclinic form of Fe$^{III}_2$ (SO$_4$)$_3$ (Table 1). The large quadrupole splitting (ΔEq) value for Fe^{II} reflects large electric field gradient (EFG) around the Fe nucleus. This is a general trend of the high-spin state of Fe^{II}, in which d-electrons make asymmetric electronic configuration in distorted octahedral geometries. While in this system, systematic differences due to change of geometrical distortion of the Fe environment were not obvious after careful overlooking of Table 1.

The electrochemical properties of $Na_{0.89}Fe_{1.8}(SO_4)_3$ were studied with half-cells with Li-metal anode. Note that all the measurements were started from discharging. An initial open-circuit voltage was as high as 3.92 V (vs. Li/Li$^+$) and a couple of reversible Fe^{3+}/Fe^{2+} redox waves around 3.75 V were observed in the cyclic voltammograms (inset of Fig. 2a). The average voltage of 3.75 V (vs. Li/Li$^+$) in the Li

Table 1
Refined Mössbauer spectrum parameters of pristine $Na_{2.4}Fe_{1.8}(SO_4)_3$, oxidized compounds of $Na_{1.14}Fe_{1.8}(SO_4)_3$, $Na_{1.03}Fe_{1.8}(SO_4)_3$, $Na_{0.89}Fe_{1.8}(SO_4)_3$, and its 1st discharged product in lithium half cell, where δ is isomer shift, ΔE$_q$ is quadrupole splitting and Γ is line width respectively.

		δ/mm s^{-1}	ΔE$_q$/mm s^{-1}	Γ/mm s^{-1}	Fraction, %	Normalized χ^2
$Na_{2.4}Fe_{1.8}(SO_4)_3$	Fe^{2+} (1)	1.278(6)	2.403(4)	0.424(2)	57.2	2.04
	Fe^{2+} (2)	1.286(8)	2.011(5)	0.424(2)	42.8	
$Na_{1.14}Fe_{1.8}(SO_4)_3$	Fe^{2+}	1.249(4)	2.710(8)	0.618(12)	30.2	1.51
	Fe^{3+}	0.491(10)	0.611(17)	0.424(3)	69.8	
$Na_{1.03}Fe_{1.8}(SO_4)_3$	Fe^{2+}	1.239(7)	2.735(14)	0.698(2)	24.0	1.56
	Fe^{3+}	0.487(11)	0.627(19)	0.445(3)	76.0	
$Na_{0.89}Fe_{1.8}(SO_4)_3$	Fe^{2+}	1.260(4)	2.780(8)	0.507(10)	15.8	2.42
	Fe^{3+}	0.483(6)	0.604(9)	0.452(15)	84.2	
Discharged-product in lithium half cell	Fe^{2+}(1)	1.242(7)	1.825(14)	0.519(11)	53.5	1.67
	Fe^{2+}(2)	1.220(8)	2.536(14)	0.496(8)	39.9	
	Fe^{3+}	0.438(5)	0.459(6)	0.478(2)	6.6	