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Synthesis by Electrospinning and Electrochemical Properties of $Na_2Fe_2(SO_4)_3$ Nanofibers as a Cathode Material for Sodium-Ion Batteries

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Alluaudite-type $Na_{2+2x}Fe_{2-x}(SO_4)_3$ is a promising cathode material for sodium-ion batteries because of its high voltage, low cost, and feasible synthesis at low temperature. However, it has a low ionic conductivity (1×10^{-7} S/cm) and electrical conductivity (2×10^{-9} S/cm). In this study, we improved the ionic conductivity by using electrospinning to activate ion diffusion. We also improved the electrical conductivity by using poly(vinylpyrrolidone) to form a carbon coating. Scanning electron microscopy revealed that the synthesized material consisted of nanofibers with sizes of approximately 400–800 nm. The surface area was measured by using atomic force microscopy. An X-ray Diffraction analysis was carried out to determine the structure of the $Na_2Fe_2(SO_4)_3$ nanofibers. Additionally, the initial charge-discharge capacities of $Na_2Fe_2(SO_4)_3$ were found to be 22.27 mAh/g and 19.39 mAh/g, respectively, at a current density of 0.1 C-rate.

Keywords: Na-ion batteries, Cathode material, $Na_{2+2x}Fe_{2-x}(SO_4)_3$, Electrospinning
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I. INTRODUCTION

Lithium-ion batteries (LIBs) are a major component of electronic devices, electrical/hybrid vehicles, and electric energy storage systems. However, lithium resources are limited, which raises lithium's cost and lowers its availability. Thus, finding an alternative to lithium and developing sustainable secondary batteries are imperative [1–3]. Sodium-ion batteries (SIBs) should be an excellent alternative because of sodium's abundance and low cost. Furthermore, the electropositive property of Na is close to that of Li. Therefore, SIBs, owing to their cost, safety and sustainability, can replace LIBs [2–4].

High-voltage cathode materials are mainly comprised of layered oxides and polyanion compounds (phosphates, sulfates, pyrophosphates, mixed poly-anions, fluorophosphates, *etc.*). Among them, sulfate materials are very promising as high voltage cathodes in SIBs, especially when combined with Fe (also an abundant and inexpensive metal) [5,6]. The alluaudite-type $Na_{2+2x}Fe_{2-x}(SO_4)_3$ has been noted for its high potential of Fe^{3+}/Fe^{2+} redox couples (3.8 V) and moderate capacity (≈100 mAh/g) since it was first reported by Yamada *et al.* in 2014. A significant advantage of $Na_{2+2x}Fe_{2-x}(SO_4)_3$ is its low temperature synthesis (≈ 350 °C) [5,7].

Nonetheless, the low ionic conductivity (1×10^{-7} S/cm) and electronic conductivity (2×10^{-9}) of $Na_{2+2x}Fe_{2-x}(SO_4)_3$ greatly limits its electrochemical performance [8]. Several strategies for improving its ionic and electronic conductivities have been proposed, most of which are based on solid-state, ionothermal, and simulation studies. The synthesized material is a micro-sized spherical particle [9–11].

In this study, we used electrospinning to improve the ionic conductivity by activating ion diffusion, and we formed a carbon coating with poly(vinylpyrrolidone) (PVP) to improve the electrical conductivity. We synthesized $Na_2Fe_2(SO_4)_3$ nanofibers with 400- to 800- nm diameters by using the electrospinning method and analyzed their novel properties regarding a newly-observed nano-web shape. After the sol-gel precursor had been prepared, nano-sized $Na_2Fe_2(SO_4)_3$ was synthesized by using electrospinning, and the structure surface and electrochemical properties were comprehensively analyzed [12,13]. $Na_2Fe_2(SO_4)_3$ synthesis by using electrospinning has not been previously reported.

II. EXPERIMENTAL

1. Preparation of Electrospinning Solution

Precursors were prepared by using the sol-gel method, and $Na_2Fe_2(SO_4)_3$ nanofibers were prepared by using electrospinning. Sodium sulfate (Na_2SO_4, Sigma-

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Aldrich, ≥99.0%), hydrate iron sulfate ($FeSO_4 \cdot 7H_2O$, Sigma-Aldrich, ≥99.0%), poly(vinylpyrrolidone) (PVP, Sigma-Aldrich, $M_w = 1{,}300{,}000$) were dissolved in a composite solvent to prepare a sol-gel solution. The composite solvent was prepared using distilled water (H_2O, 98%) and sulfuric acid (Sigma-Aldrich, ≥95%) in a constant ratio. The mixture was stirred for 24 h at 100–200 rpm.

2. Electrospinning

The prepared solution was placed in a plastic capillary. A stainless steel alloy was used as a collector. The distance between the capillary and the collector was set at 15 cm, and the applied voltage was 15–22 kV. The nanofibers were deposited on the collector, which was dried at 100 °C for 24 h. The dried fibers were pre-calcined at 200 °C for 2 h, and then calcined at 400 °C for 6 h in an Ar atmosphere at a 0.5 °C/min heating rate and with a higher gas flow rate.

3. Characterization

X-ray diffraction (XRD) patterns for the cathodes were obtained using a Siemens D-5000 diffractometer in the 2θ range from 10 to 70° with Cu Kα radiation (λ = 1.54068 Å). The morphology of the obtained powder was observed using scanning electron microscopy (SEM).

Regarding the electrochemical testing, the cathode was fabricated by blending 60% active material, 20% super P carbon black, and 20% binder in *N*-methyl-2-pyrrolidone. The mixed slurry was cast uniformly on a thin Al foil and dried in vacuum for 12 h at 120 °C. After the film had been dried, it was pressed by using a pressing machine. The pressure was 35 kgf/cm^2.

The electrochemical performance was measured using a CR2032 coin-type cell. Sodium-metal foil was used as the anode. A Whatman glass fiber membrane and a 1-M Na $NaClO_4$ electrolyte solution dissolved in a propylene carbonate (PC) were used as the separator and the electrolyte, respectively. The cells were assembled in an argon-filled glove box. Electrochemical tests were performed at voltages between 2.0 and 4.5 V. The frequencies were changed from 0.001 Hz to 0.1 MHz, and the amplitude of the alternating-current signal 10 mV. Nyquist plots (Z' *vs.* $-Z''$) were prepared and analyzed using the Z-plot and the Z-view packages.

III. RESULTS AND DISCUSSION

Figure 1 shows (a) an optical microscope image and (b) a SEM image of the precursor of $Na_2Fe_2(SO_4)_3$. After calcination, the fiber shape was maintained, and nano-sized primary particles could be observed. The fiber had a smooth fiber shape with a diameter of 400–800 nm, and a nano-web shape.

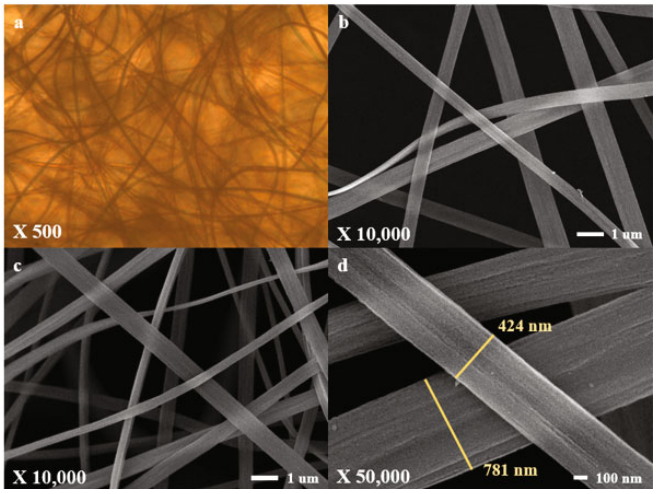

Fig. 1. (a) Optical microscope image and (b) SEM image of the precurcor. (c)–(d) SEM images of the $Na_2Fe_2(SO_4)_3$ cathode material.

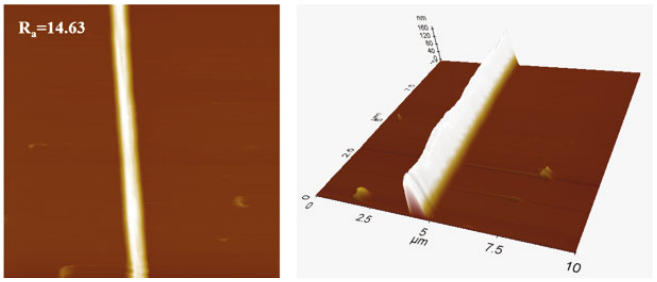

Fig. 2. AFM images of the $Na_2Fe_2(SO_4)_3$ nanofibers.

Figure 2 shows a atomic force microscopy (AFM) image of a $Na_2Fe_2(SO_4)_3$ nanofiber after calcination at 400 °C. The AFM data demonstrate the roughness of the nanofiber. The roughness of the nanofiber was 14.63 nm.

Figure 3 show (a) XRD patterns and (b) the FT-IR spectrum, respectively. The XRD patterns (a) were used to investigate the crystal structures of the $Na_2Fe_2(SO_4)_3$ cathode material. The diffraction peaks showed some impurities, but most of them agreed with those in other reports [5,14,15]. The impurities were mainly found in α-$FeSO_4$. FT-IR was performed to analyze carbon's binding form. In the spectrum, the peak at ∼1730 cm^{-1} could be attributed to C=O (carbonyl and carboxyl) [5, 16]. This shows that the carbon coating is formed by PVP and that the carbon band is a double bond. The presence of sulfate compound was confirmed by the observed SO_4^{-2} peaks.

Figure 4 shows (a) the initial charge-discharge curves and (b) dQ/dV for the $Na_2Fe_2(SO_4)_3$ electrodes at a current density of 0.1C between 2.0 and 4.5 V. The initial charge-discharge capacities of $Na_2Fe_2(SO_4)_3$ are 22.27

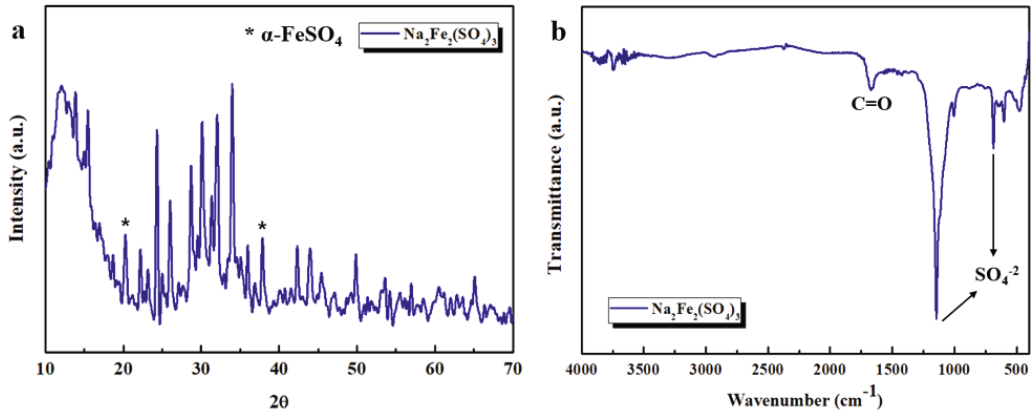

Fig. 3. (a) XRD pattern and (b) FT-IR spectrum for the $Na_2Fe_2(SO_4)_3$ cathode material.

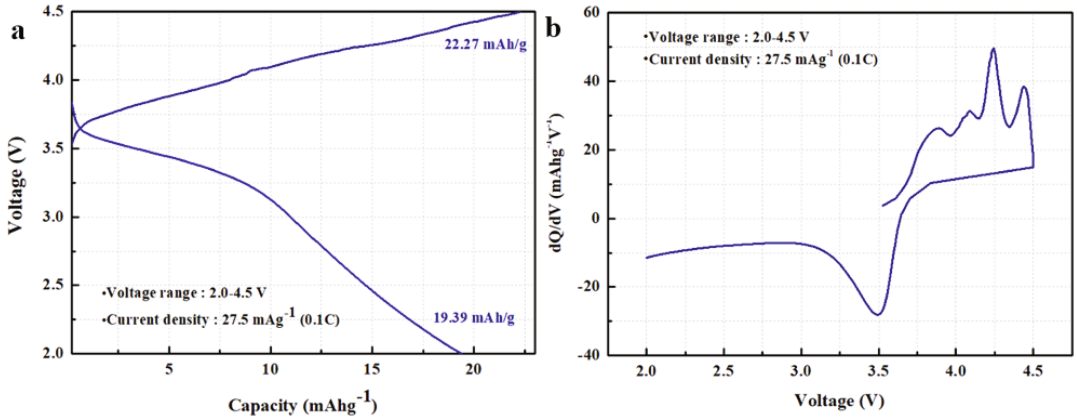

Fig. 4. (a) Initial charge/discharge curves and (b) dQ/dV curves for the cathode material.

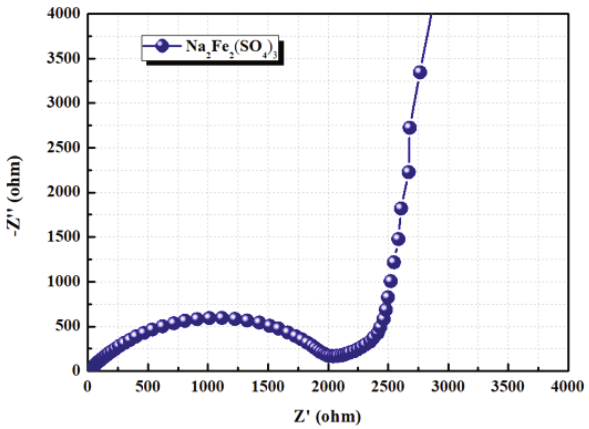

Fig. 5. Impedance spectrum of the $Na_2Fe_2(SO_4)_3$ electrodes after the 1st cycle.

and 19.39 mAh/g, respectively, at room temperature.

Figure 5 shows the AC impedance spectrum of the $Na_2Fe_2(SO_4)_3$ electrode. In the impedance curves, all curves contain depressed a semicircle in the high-frequency range and a straight line in the low-frequency range, respectively. The depressed semicircle indicates a resistance to charge transfer, and the straight lines occur due to ion diffusion at the electrode-electrolyte interface. R_s represents the electrolyte resistance, and R_{ct} represents the charge-transfer resistance between the electrolyte and the electrode. The Warburg resistance W_o is also associated with Na^+ diffusion from the $Na_2Fe_2(SO_4)_3$ electrode [5, 17, 18]. The R_{ct} of the $Na_2Fe_2(SO_4)_3$ electrode was measured to be 2083 Ω. The Na ion conductivity was calculated using the following equation [19]:

$$\sigma = \frac{d}{AR}$$

where d is the disk thickness, A is disk area, and R is the electrode resistance. The calculated value is 1.48×10^{-6} S/cm.

IV. CONCLUSIONS

$Na_2Fe_2(SO_4)_3$ nanofibers were prepared by using the electrospinning method. The nano-web structure im-

proved the ionic conductivity by activating ion diffusion, and the carbon coating with PVP improved the electrical conductivity. SEM images confirmed that a nanofiber-shape cathode material had been synthesized. The diameters of the nanofibers were found to range from 400 to 800 nm and the roughness was 83.56 nm. Also, the binding form of carbon was confirmed through FT-IR spectroscopy. The conductivity of the Na ion in $Na_2Fe_2(SO_4)_3$ was examined using AC impedance spectroscopy, and the calculated value was 1.48×10^{-6} S/cm. In this study, the cathode material could not be stably synthesized because impurities were introduced. However, if the electrospinning synthesis conditions are established, $Na_2Fe_2(SO_4)_3$ with a uniform shape should be able to be synthesized. Therefore, high output characteristic can be expected.

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