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A supercritical methanol route for the synthesis of sodium iron oxide submicron plates for use as a cathode material for sodium-ion batteries

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ABSTRACT

Highly crystalline, phase-pure $NaFeO_2$ submicron plates are synthesized using a facile and simple supercritical methanol route. The synthesized $NaFeO_2$ submicron plates are 160 to 680 nm in width and 90 nm in thickness. Because of their two-dimensional structure, the $NaFeO_2$ submicron plates exhibit excellent electrochemical performance with smaller polarization compare to micron-sized $NaFeO_2$ particles synthesized using a solid-state method; the initial charge capacity is 94 mAh g^{-1} at 10 mA g^{-1} and high-rate capacity of 34 mAh g^{-1} at 50 mA g^{-1}, which is 180% higher than that of solid-state synthesized $NaFeO_2$. The enhanced charge-discharge characteristics are attributed to the low charge transfer resistance and high Na-ion diffusivity.

1. Introduction

Sodium-ion batteries (SIBs) are considered the most promising alternative to LIBs because of the abundance and uniform distribution of sodium [1]. The incorporation of iron into the electrode materials is one of the most promising design approaches for large-scale battery applications because of the abundance, nontoxicity, and environmental benignity of iron [2]. However, The utilization of the Fe^{3+}/Fe^{4+} redox potential in LIBs has been unsuccessful because of instability of Fe^{4+} in the oxide and the decomposition of the electrolytes at high potentials [3].

The possibility of utilizing the Fe^{3+}/Fe^{4+} redox couple in SIBs has been investigated for the last two decades in the form of layered α-$NaFeO_2$ [4], but only very few studies have reported the reversible capacity of SIB cathodes based on the Fe^{3+}/Fe^{4+} redox couple [5,6]. Generally, $NaFeO_2$ is synthesized using a solid-state method [6–9], and although the solid-state method is simple and it is easy to achieve the correct stoichiometry of the electrode material, it is difficult to control the morphology of particles (e.g., size, shape, and surface area), which is an important factor determining the electrochemical performance of the active materials. In this study, we report a facile method, using supercritical methanol (scMeOH), to obtain $NaFeO_2$ submicron plates with enhanced electrochemical performance.

2. Experimental

The $NaFeO_2$ were synthesized in scMeOH (designated as scNFO) using a tube reactor (volume of 11 mL). Various molar ratios of NaOH (purity > 95%, Sigma-Aldrich, 0.3, 0.35, 0.4 M) to $Fe(NO_3)_3 \cdot 9H_2O$ (Daejung Chemicals & Metals Co., 0.1 M) were dissolved in methanol separately. Then, the solutions were mixed together with vigorous stirring and 4 mL of the mixed solution was transferred into the reactor. The reactor was dipped into the salt bath (400 °C) for 10 min. After that, it was quenched in a cold-water bath. The formed particles were collected and washed with ethanol and centrifuged, filtered, and vacuum dried at 70 °C overnight. The collected sample was heat-treated at 700 °C /2 h under N_2 flow (60 mL min^{-1}). In addition, $NaFeO_2$ particles were synthesized using a solid-state (designated as ssNFO) for comparison purpose. Stoichiometric amounts of Na_2O_2 and Fe_3O_4 were mixed using ball milling and sintered at 650 °C/12 h under air flow.

The synthesized particles were characterized using scanning electron microscopy (FE-SEM, JSM7401F, JEOL), high-resolution transmission electron microscope (HR-TEM, JEM-2100F, JEOL), and X-ray diffraction (XRD, D8ADVANCE, Bruker Corporation). The electrochemical properties were measured in CR2032-type coin cells. The working electrode was composed of 70 wt% active material, 10 wt% acetylene black, and 20 wt% Polyvinylidene

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fluoride in *N*-methyl-2-pyrrolidone. The slurry was cast on an Al foil and was punched into 14-mm diameter discs (active material loading 1.4–2.1 mg cm^{-2}). The cells were assembled with the composite cathode, sodium metal (counter electrode), and a glass fiber filter (Whatman GF/B, pore size 1 μm, Whatman) as the separator. The electrolyte was 1 M $NaClO_4$ dissolved in a polycarbonate (PC)/ethylene carbonate (EC)/dimethyl carbonate (DMC) solvent (volume ratio of PC:EC:DMC = 1:1:1). Cyclic voltammetry (CV) on the cells were performed using a model ZIVE MP1 potentiostatic analyzer (WonATech Co.). The CV were performed at scanning rates of 0.1 mV s^{-1} in a voltage window of 2.5–3.5 V (hereafter vs. Na^+/Na). The cells were galvanostatically charged and discharged using a model WBCS3000 battery test system (WonATech Co.) at room temperature. Electrochemical impedance spectroscopy (EIS) tests were performed using a ZIVEMP1 impedance analyzer (WonATech Co.) over the range of 100 kHz–10 mHz at 2.5 V.

3. Results and discussion

The XRD patterns of the scNFO samples with different precursor ratios are shown in Fig. 1a. At a low Na:Fe ratio of 3:1 (Na-deficient conditions), Fe_2O_3 impurities were observed, while at a high Na:Fe ratio of 4:1 (Na-sufficient condition), Na_2CO_3 impurities were found in the patterns. The X-ray diffraction pattern of the scNFO particles synthesized using a Na:Fe ratio of 3.5:1 well-matched that of O3–type layered $NaFeO_2$ (JCPDS No. 82-1495) without Fe_2O_3 and Na_2CO_3 impurities. The strong and sharp Bragg peaks indicate the formation of highly crystalline $NaFeO_2$ particles. The crystallite size of scNFO, calculated using $2\theta = 16°$ and the Scherer equation, was 108 nm. This value is much smaller than that of ssNFO (480 nm). The Rietveld refinement of the XRD patterns (shown in Fig. 1b) indicates that no impurities were present. As indicated by the arrows in the figure, 4.5% of the β-$NaFeO_2$ phase

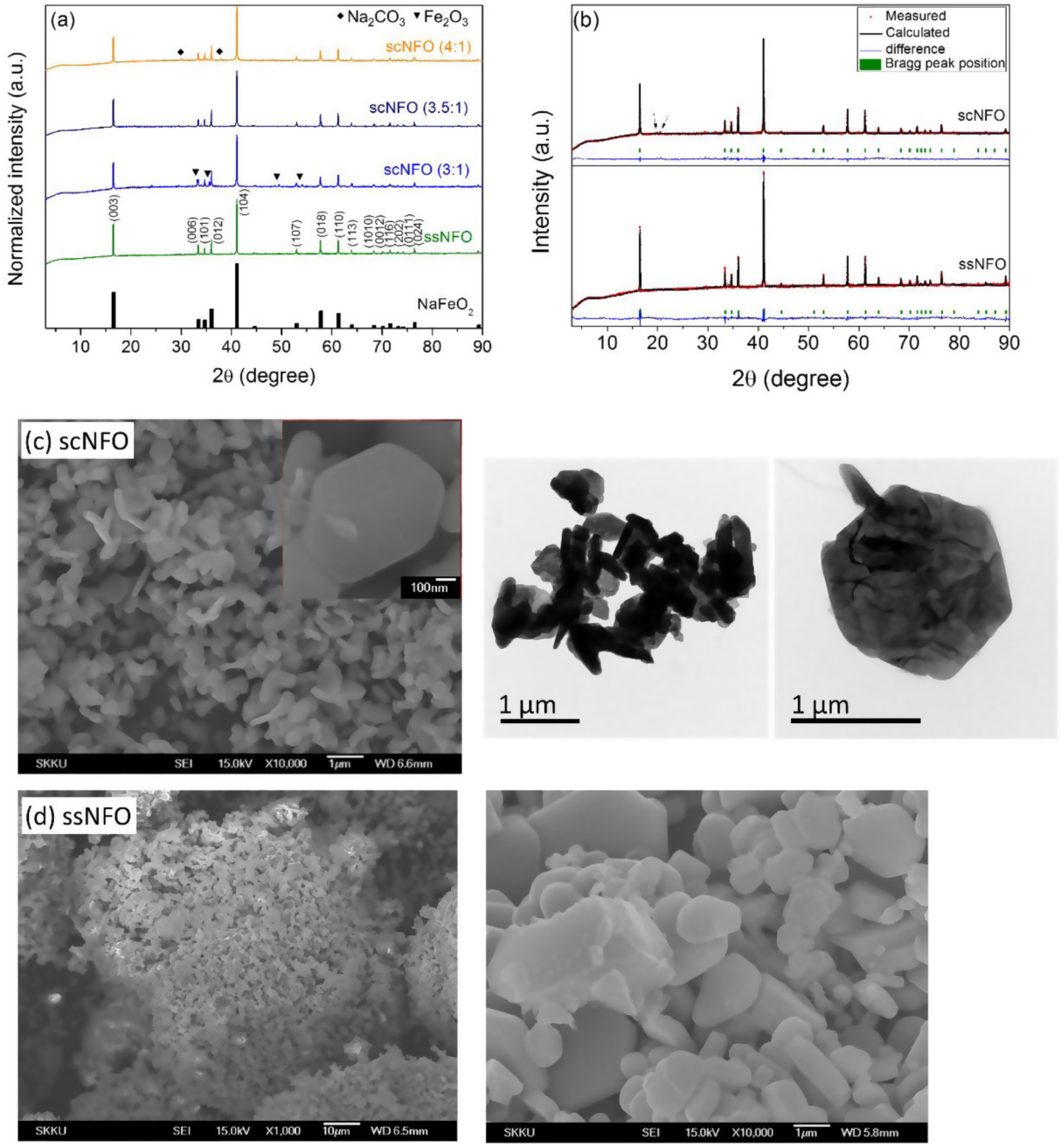

Fig. 1. (a) XRD patterns, (b) Rietveld analysis, SEM and TEM images of (c) scNFO, and SEM images of (d) ssNFO.