Journal of Power Sources 328 (2016) 503–509

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Bio-inspired 2-line ferrihydrite as a high-capacity and high-rate-capability anode material for lithium-ion batteries

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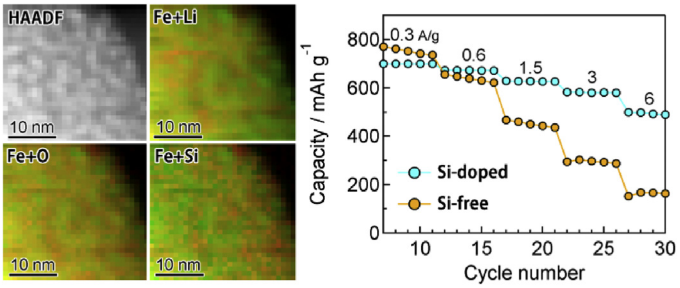
HIGHLIGHTS

- Si-doped iron oxyhydroxides were prepared inspired by a bacteriogenic product.
- The materials showed high capacity and high rate capability.
- Si-doping enhanced rate capability of the iron oxyhydroxide.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 April 2016
Received in revised form
1 August 2016
Accepted 8 August 2016

Keywords:
Bacteriogenic iron-based oxide
2-Line ferrihydrite
Si-doped 2-line ferrihydrite
Lithium-ion batteries

ABSTRACT

A high-capacity and high-rate-capability anode material for lithium-ion batteries, silicon-doped iron oxyhydroxide or 2-line ferrihydrite (2Fh), was prepared by mixing iron nitrate powder, tetraethyl orthosilicate, 2-propanol, and ammonium hydrogen carbonate powder at room temperature. The design of this material was inspired by a bacteriogenic product, a nanometric amorphous iron-based oxide material containing small amounts of structural Si. The atomistic structure of the prepared Si-doped 2Fh was strongly affected by the Si molar ratio [$x = \mathrm{Si}/(\mathrm{Fe} + \mathrm{Si})$]. Its crystallinity gradually decreased as the Si molar ratio increased, with a structural variation from nanocrystalline to amorphous at $x = 0.25$. The sample with $x = 0.20$ demonstrated the best Li storage performance. The developed material exhibited a high capacity of ~400 mAh g^{-1} at the 25th cycle in the voltage range of 0.3–3.0 V and at a current rate of 9 A g^{-1}, which was three times greater than that of the Si-free 2Fh. This indicates that Si-doping into the 2Fh structure realizes good rate capability, which are presumably because of the specific nanocomposite structure of iron-based electrochemical centers embedded in the Si-based amorphous matrix, generated by reversible Li insertion/deinsertion process.

1. Introduction

Li-ion batteries are used as a power supply for various electric devices. They mainly comprise as an anode, an electrolyte, a separator, and a cathode, and the key components determining

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http://dx.doi.org/10.1016/j.jpowsour.2016.08.037
0378-7753/

their performance are the electrode materials [1–8]. Recently, with the expanding use of Li-ion batteries for electrical vehicles, hybrid cars, and even for airplanes, additional property enhancement, such as energy density, power density, and safety, is strongly demanded in various fields. Development of next generation electrode materials with excellent rate capabilities and cyclabilities is a smart solution. The most common anode material in the current Li-ion battery system is graphite [9], which has a theoretical capacity of 372 mAh g^{-1}. Although this material has excellent properties, optimization of this system has been thoroughly conducted, closely reaching a limit of property enhancement. Iron-based oxide materials, such as FeO, α-Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4, are possible candidates for anode materials because of their high capacity (reaching nearly 1000 mAh g^{-1}), cost-effectiveness, and environmental-friendliness [10–19]. However, nanosizing, nanostructuring, and/or hybridization with carbon materials, which all contain complicated fabrication processes, are necessary to obtain good rate capabilities and cyclabilities.

We have focused on a qualitatively different iron-based oxide, which is naturally created by a species of aquatic iron-oxidizing bacteria, *Leptothrix ochracea* [20,21]. The bacteriogenic material comprises 3-nm-diameter primary particles containing three inorganic components, Fe^{3+}, Si^{4+}, and P^{5+}, evenly distributed at an atomic ratio of 73:22:5, respectively [22]. Its atomistic structure is amorphous and the X-ray diffraction pattern is similar to that of 2-line ferrihydrites (2Fhs), which are nanocrystalline iron oxyhydroxides [23]. Moreover, the bacteriogenic material has a unique nano/micro-hierarchical structure. The primary nanoparticles assemble into secondary structures of fibrils and globules and these secondary structures are intricately interconnected into microtubules of ~1 μm in diameter [22].

Previously, we carefully investigated the electrochemical performance of the bacteriogenic material and showed that it exhibits a reasonably good rate capability in the high voltage range of 1.5–4.0 V. The discharge capacity exceeded 70 mAh g^{-1} at a very high current rate of 1.67 A g^{-1} [24]. The nanometric, compositional, and amorphous features of the material most likely contribute to the efficient in- and out-diffusion of Li ions. The presence of covalent and robust Si–O and P–O tetrahedra may also lead to the flexible response to repeated Li insertion/deinsertion processes [24]. We also found that the bacteriogenic material works as a high capacity and high rate-capability $Fe^{3+} \rightleftharpoons Fe^0$ conversion anode material (~900 mAh g^{-1}) at a low voltage range of 0–3 V [22]. Interestingly, the original amorphous structure, which is constructed of a continuous framework of FeO_6 octahedra and isolated SiO_4 tetrahedra [23], was completely decomposed through the first discharge process to a nanocomposite, in which ~2-nm-diameter α-Fe-like particles were embedded in an amorphous Si- and P-oxide matrix storing Li ions [22]. The good rate capability and cyclability appear to result from the nanocomposite of the Fe-core/Si, P, (Li) matrix, which prevents the Fe-cores from undesirable aggregation. The additional Si and P components obviously play an important role in the rate capability and cyclability.

In our recent work, inspired by the bacteriogenic iron-based oxide material, we synthesized Si-doped, nanometric, and amorphous iron oxyhydroxides with similar particle size and ionic structure to the bacteriogenic material using a conventional coprecipitation method [25]. We found that the Si-doped 2Fh with an appropriate amount of Si showed a reasonably good rate capability in a high voltage range of 1.5–4.0 V. However, the potential of Si-doped 2Fhs for high capacity conversion anode materials has not previously been investigated. Here, we synthesized the Si-doped 2Fhs by a very simple method and investigated the effect of Si-doping on their electrochemical performance in a low voltage range of 0–3.0 V.

2. Experimental

2.1. Sample preparation and characterization

Si-doped samples were prepared by modifying the report of Smith et al. [26]. First, 0.05 mol of $Fe(NO_3)_3 \cdot 9H_2O$ (Nacalai Tesque, 99.0%) was crushed to a fine powder by an alumina mortar and pestle and dissolved in 10 mL of 2-propanol (Nacalai Tesque, 99.0%). An appropriate amount of tetraethyl orthosilicate (TEOS, Nacalai Tesque 95.0%) was added to the solution. The Si concentration, $x = Si/(Si + Fe)$, was adjusted such that $x = 0$–0.50 in 0.05 increments. Then, 0.6 mol of NH_4HCO_3 (Nacalai Tesque 96.0%) was added to the solution and mixed using an alumina pestle until the rate of CO_2 generation was quite slow and a thick, red ocher paste formed. The obtained paste was moved to a polytetrafluoroethylene (PTFE) beaker and left for ~6 h at room temperature to complete the reaction. After that, the paste was washed with ~2 L of distilled water and ~200 mL of ethanol and dried under vacuum for 2–3 days at room temperature. Elemental analysis of each sample was performed via X-ray fluorescence spectroscopy (XRF; ZSX PrimusII; Rigaku, Japan). The crystallographic structures and microstructures of the samples were characterized using X-ray diffractometry (XRD; RINT-2000; Rigaku, Japan and BL04B2 at the SPring-8, Hyogo, Japan), transmission electron microscopy (TEM; JEM-2100F; JEOL, Japan), and scanning transmission electron microscopy (STEM; JEM-2100F with CEOS C_s-corrector; JEOL, Japan) in conjunction with electron energy-loss spectroscopy (EELS; GIF Tridiem; Gatan, Germany). The chemical binding states of the samples were determined using Fourier transform infrared spectroscopy (FTIR; Nicolet 6700; Thermo Scientific, USA).

2.2. Electrochemical measurements

Half cells (2032 coin-type) were fabricated to evaluate the electrochemical performance of the samples. Assembly of the half-cells was performed in an Ar-filled glove box. Li metal foil (Honjo Metal), 1 mol dm^{-3} $LiPF_6$ solution in a 3:7 v/v mixture of ethylene carbonate/diethyl carbonate (EC/DEC) (Tomiyama Chemicals), and a borosilicate glass fiber sheet (Whatman GF/D) were used as the counter electrode, electrolyte, and separator, respectively. The working electrode comprised 70 wt% Si-doped 2Fh samples ($x = 0$–0.30 in 0.05 increments), 14 wt% electrical conducting material (KETJENBLACK ECP from Lion), 6 wt% electrical conducting material (vapor-grown carbon fiber (VGCF) from Showa Denko), and 10 wt% binder (polyvinylidene fluoride (PVDF; Kureha)). The 2Fh samples were dried under vacuum at 120 °C for 18 h prior to use. Each dried 2Fh sample and ECP were mixed via ball-milling (400 rpm, 3 h), and the mixed powder was dried again under vacuum at 120 °C for 2 h. The mixed powder of 2Fh and ECP, VGCF, and PVDF was dissolved in N-methylpyrrolidone (NMP; Sigma-Aldrich) and spread on copper foil current collectors. The obtained sheets were dried at 120 °C in a vacuum overnight. Each sheet prepared with an Si-doped 2Fh sample was then cut into a 16 mm disk. The cell performance was evaluated using an electrochemical analyzer (Toscat2000; Toyo system, Japan) under galvanostatic conditions in the voltage range of 0.3–3.0 V at 0.1–12 A g^{-1}. The rate capability of the 2Fh samples were measured at current rates of 0.1, 0.3, 0.6, 1.5, 3, 6, 9, and 12 A g^{-1}. For electrochemical impedance spectroscopy (EIS), half-cell prepared with the sample with $x = 0$ and 0.20 were discharged and charged repeatedly 30 cycles in a voltage range of 0–3.0 V at a current rate of 9 A/g, after reaching open circuit voltage state, ELS was measured on a potentionstat–galvanostat (Biologic, VMP3) with an alternating current (AC) amplitude of 10 mV for frequencies from 50 mHz to 1 MHz. For *ex-situ* TEM measurements, a half-cell after