$\epsilon$-FeOOH: A Novel Negative Electrode Material for Li- and Na-Ion Batteries

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ABSTRACT: The demand for eco-friendly materials for secondary batteries has stimulated the exploration of a wide variety of Fe oxides, but their potential as electrode materials remains unknown. In this contribution, $\epsilon$-FeOOH was synthesized using a high-pressure/high-temperature method and examined for the first time in nonaqueous Li and Na cells. Under a pressure of 8 GPa, $\alpha$-FeOOH transformed into $\epsilon$-FeOOH at 400 °C and then decomposed into $\alpha$-Fe$_2$O$_3$ and H$_2$O above 500 °C. Here, FeO$_6$ octahedra form [2 × 1] tunnels in $\alpha$-FeOOH or [1 × 1] tunnels in $\epsilon$-FeOOH. The $\epsilon$-FeOOH/Li cell exhibited a rechargeable capacity ($Q_{\text{ach}}$) of ~700 mA h g$^{-1}$ at 0.02–3.0 V, whereas the $\epsilon$-FeOOH/Na cell indicated a $Q_{\text{ach}}$ of less than 30 mA h g$^{-1}$ at 0.02–2.7 V. The discharge and charge profiles of $\epsilon$-FeOOH and $\alpha$-FeOOH were similar, but the rate capability of $\epsilon$-FeOOH was superior to that of $\alpha$-FeOOH.

INTRODUCTION

With the growing market for secondary batteries, the abundance of resources for these batteries and their eco-friendliness are becoming crucial issues for building a sustainable society. Electrode materials consisting of Fe oxides are a possible solution because Fe has the fourth highest Clark number and low toxicity. Since the commercialization of lithium-ion batteries (LIBs), various Fe oxides such as FeOOH,1–10 LiFeO$_2$,12 LiFe$_2$O$_4$,10 Fe$_3$O$_4$,18,22 and FeO$_{1+\delta}$Cl$_x$ have been proposed. Among these Fe oxides, FeOOH has especially attracted attention as a negative electrode material for LIBs1–6,10,11 or as a catalyst for Li–O$_2$ batteries.4,10 Furthermore, FeOOH has been utilized as a precursor to synthesize FeO$_2$ and Fe$_2$O$_3$ powders, exhibiting interesting particle morphologies.

FeOOH includes several polymorphs, as illustrated in Figure 1.26–29 For example, $\alpha$-FeOOH (goethite) crystallizes into an orthorhombic structure with the $Pnma$ space group, building [2 × 1] tunnels (Figure 1a).26 LIBs with $\alpha$-FeOOH nanorods with a length of 100–200 nm and a diameter of ~40 nm indicated a rechargeable capacity ($Q_{\text{ach}}$) of ~600 mA h g$^{-1}$ at 0.01–3.0 V versus Li$^+/\text{Li}$. Meanwhile, $\beta$-FeOOH (akaganeite) possesses a tetragonal structure with the $I4/m$ space group, forming two types of [2 × 2] and [1 × 1] tunnels (Figure 1b).27 The chemical formula of $\beta$-FeOOH is specifically represented as FeO$_{1-x}$(OH)$_{1+y}$Cl$_y$, where Cl$^-$ ions lie at the center to maintain the [2 × 2] tunnels.27 The electrochemical properties of $\beta$-FeOOH strongly depend on its particle morphologies and particle sizes.5,7 Yu et al. reported that the $Q_{\text{ach}}$ of LIBs with nano-sized $\beta$-FeOOH reached ~1400 mA h g$^{-1}$.7 However, the mechanism underlying this large $Q_{\text{ach}}$ is a debatable subject because the maximum theoretical capacity ($Q_{\text{theo}}$) of FeOOH is limited to 746.1 mA h g$^{-1}$ by the following reactions

$$\text{FeOOH} + 3\text{Li}^+ + 3e^- \rightarrow \text{Fe}^0 + \text{Li}_2\text{O} + \text{LiOH}$$

for the initial decomposition reaction and

$$\text{Fe}^0 + \text{Li}_2\text{O} \leftrightarrow \text{Fe}^{2+}\text{O} + 2\text{Li}^+ + 2e^-$$

for the subsequent charge and discharge reactions. As shown in Figure 1c, $\gamma$-FeOOH (lepidocrocite) exhibits a zigzag layer structure with the $Cmcm$ space group30 and has thus been employed as a precursor to synthesize FeOCl$^1$ or FeOOLi$^{1,12}$ via ion exchange reactions. As a positive electrode material, FeOOLi resulted in a $Q_{\text{ach}}$ of ~90 mA h g$^{-1}$.12 The crystal structure of $\delta$-FeOOH depends on the material origins or preparation methods, and thus, several structural models have been proposed.28–31 The average structure of $\delta$-FeOOH is usually interpreted to be hexagonal with the $P\bar{6}_3m1$ space group, as shown in Figure 1d.

In contrast to $\alpha$, $\beta$, $\gamma$, and $\delta$-FeOOH, another isomorph, namely, $\epsilon$-FeOOH, is obtained at high pressures above 5 GPa.

Received: February 19, 2020
Accepted: April 6, 2020
Published: April 20, 2020
and temperatures above 200 °C,32,33 and it crystallizes into an orthorhombic structure with the Pmn21 space group. As shown in Figure 1e, ϵ-FeOOH forms [1×1] tunnels through edge-sharing FeO6 octahedra. The crystal structure of ϵ-FeOOH can be regarded as a distorted rutile structure, and it is similar to those of InOOH, β-CrOOH (guyanaite), and GaOOH.34−36 In the field of geochemistry, ϵ-FeOOH and even higher-pressure phases have received a great deal of attention,37,38 but to our best knowledge, the electrochemical properties of ϵ-FeOOH remain unknown.

According to the true density, that is, the density determined via powder X-ray diffraction (XRD) measurements (dXRD), dXRD of ϵ-FeOOH (∼4.44 g cm−3)32,33 is greater than that of α-FeOOH (∼4.18 g cm−3),26 β-FeOOH (∼3.58 g cm−3),27 or γ-FeOOH (∼4.00 g cm−3).28 This allows increasing the volumetric energy density of LIBs, which is an important performance metric. Moreover, determining the electrochemical properties of ϵ-FeOOH provides an in-depth understanding of the relationship between crystal structures and electrochemical properties, which is essential to designing future eco-friendly electrode materials. We thus synthesized ϵ-FeOOH using a high-pressure/high-temperature (HP/HT) method and examined its electrochemical properties in nonaqueous Li cells. In addition, we investigated the electrochemical properties in nonaqueous Na cells because Na is more abundant than Li. To our best of our knowledge, this is the first time this electrode material has been demonstrated in LIBs and sodium-ion batteries (NIBs).

■ RESULTS AND DISCUSSION

Figure 2a shows the XRD pattern of the pristine α-FeOOH sample. The crystal structure of α-FeOOH is assigned to the orthorhombic structure with the Pmn21 space group. According to the Rietveld analysis, the lattice parameters were determined to be \( a_o = 9.9772(5) \text{ Å}, b_o = 3.0278(2) \text{ Å}, \) and \( c_o = 4.6131(3) \text{ Å}, \) which are slightly larger than those previously reported for α-FeOOH (\( a_o = 9.9134 \text{ Å}, b_o = 3.0128 \text{ Å}, \) and \( c_o = 4.5800 \text{ Å})26\). The Rietveld analysis results and structural parameters are summarized in Figure S1 and Table S1.

![Figure 1. Crystal structures of (a) α-FeOOH (goethite), (b) β-FeOOH (akaganeite), (c) γ-FeOOH (lepidocrocite), (d) δ-FeOOH (feroxyhyte), and (e) ϵ-FeOOH.](image)

![Figure 2. XRD patterns of (a) α-FeOOH (pristine) and (b)−(i) HP-/HT-treated samples in order of increasing treatment temperature from top to bottom. Red and blue stars indicate diffraction lines from ϵ-FeOOH and Fe2O3, respectively.](image)

Figure 2b−i shows the XRD patterns of the HP-/HT-treated samples in order of increasing treatment temperature. The applied pressure was 8 GPa for all the samples. The HP(100 °C), HP(200 °C), and HP(300 °C) samples maintained the α-FeOOH-type structure, although additional diffraction lines indicated by red stars (★) were observed in the HP(300 °C) sample. Here, we denote these samples by HP(XXX °C), where XXX represents the heating temperature. These additional diffraction lines originate from the γ-FeOOH phase, as described later. The lattice parameters of the α-FeOOH phase decrease with the increasing heating temperature; for instance, the parameters of HP(100 °C) decrease from \( a_o = 9.9771(11) \text{ Å} \) to \( a_o = 9.9615(5) \text{ Å} \), from \( b_o = 3.0260(4) \text{ Å} \) to \( b_o = 3.0224(1) \text{ Å} \), and from \( c_o = 4.6112(6) \text{ Å} \) to \( c_o = 4.5968(3) \text{ Å} \) for HP(300 °C). The XRD patterns of the HP(400 °C) and HP(500 °C) samples can almost be indexed to a single phase with an ϵ-FeOOH-type structure and the...
and Fe₂O₃ for HP(800 °C) samples (Figure 2g–i). The observed weight loss (≈10.5%) was consistent with the calculated weight loss described in eq 3.

Figure 3a–f shows the scanning electron microscopy (SEM) images of the pristine α-FeOOH, HP(100 °C), HP(200 °C), HP(400 °C), HP(500 °C), and HP(800 °C) samples. Field emission SEM (FE-SEM) images of only the pristine α-FeOOH sample aggregate together, forming large secondary particles. As shown in Figure 3g–i, the primary particles exhibit a needle shape with dimensions of ∼100 × 500 nm. The HP(100 °C) sample indicates a spherical secondary particle with a radius of ∼10 μm, while spherical secondary particles are partially broken in the HP(200 °C) sample. The HP(400 °C) sample, which crystallized into the ε-FeOOH-type structure, shows a large, scally-shaped secondary particle of more than 20 μm in diameter. In contrast, particles in HP(500 °C) are isolated from each other and exhibit a flat, smooth surface, as evidenced by the plate-shaped particles with a thickness of ∼200 nm and a lateral length of ∼1 μm in Figure 3i. Meanwhile, the HP(800 °C) sample atomizes into Fe₂O₃ and H₂O, as demonstrated by the thermogravimetric (TG) curve shown in Figure S3.
°C) sample exhibits nonuniform large particles of ~50 μm in size.

Above, the drastic changes in particle morphologies and particle sizes were shown to correlate with the structural changes associated with the α-FeOOH → ε-FeOOH → α-Fe₂O₃ transformation. Based on the crystallographic relationship, the Pmn₂₁ (ε-FeOOH) space group is a maximal nonisomorphic subgroup of the Pnma (α-FeOOH) space group.²⁹ On the other hand, the R₃c (α-Fe₂O₃) space group is not a minimal nonisomorphic supergroup of the Pmn₂₁ space group. Hence, the α-FeOOH structure can change to ε-FeOOH by a simple translation of Fe and O atoms, while the structural change from ε-FeOOH to α-Fe₂O₃ should be accompanied by breaking and reforming the Fe–O bonds. These drastic changes in particle morphologies and particle sizes also appeared along with the structural changes in Li[Li₁/₃Ti₅/₃]O₄, in which a spinel structure with the Pnma space group under a pressure of 12 GPa and at temperatures above 600 °C.³⁹

Figure 4 shows the discharge and charge curves of Li cells with the pristine α-FeOOH, HP(100 °C), HP(200 °C), HP(300 °C), HP(400 °C), HP(500 °C), HP(600 °C), and HP(800 °C) samples. The cells were operated at a current of 0.1 mA. The red lines in (a–h) are the discharge and charge curves at the first cycle. dQ/dV (or dQ/dQ) curves of the (i) α-FeOOH (pristine), (j) HP(400 °C), and (k) HP(800 °C) samples. The red and black lines in (i–k) are the dQ/dV (or dQ/dQ) curves at the first and second cycles, respectively.

When the discharge cutoff voltage decreases to 0.02 V, the so-called conversion reaction described in eq 2 becomes dominant, and thus, the differences between the discharge and charge profiles of the samples vanish. Because the complete conversion reaction offers a Q\text{theo} of 746.1 mA h g⁻¹, Fe ions with the monovalent state still exist in the sample based on the observed Q\text{cha} values. In general, the maximum Q\text{theo} value of FeOOH polymorphs seems to remain in the range of 600–800 mA h g⁻¹, except for nano-sized β-FeOOH. As described in the Introduction, a Q\text{theo} of more than 1000 mA h g⁻¹ cannot be explained without considering other contributions such as the capacitance of carbon additives.

To further clarify the differences between the electrochemical properties of α-FeOOH and ε-FeOOH, extended cycle tests were performed at a current of 0.3 mA over 30 cycles. Figure 5a,b shows the discharge and charge curves of Li cells with the HP(300 °C) and HP(400 °C) samples, respectively. As shown in Figure 5d,e, the major phase of HP(300 °C) was α-FeOOH, whereas that of HP(400 °C) was ε-FeOOH. For HP(300 °C), the Q\text{cha} value at the first cycle
The rapid decrease in $Q_{cha}$ at the first cycle remains at $592.8$ mA h$^{-1}$, which is $85.2\%$ of the $Q_{cha}$ value at 0.1 mA. Hence, $\epsilon$-FeOOH is found to have a better rate capability than $\alpha$-FeOOH, although its discharge and charge profiles are similar to those of $\alpha$-FeOOH. Actually, the rate capability shown in Figure S5 supported such consideration.

For both HP(300 °C) and HP(400 °C), $Q_{cha}$ and ($Q_{dis}$) rapidly decrease during the initial five cycles. At the 30th cycle, HP(300 °C) and HP(400 °C) retained 47.1 and 31.1% of their initial capacities, respectively, as shown in Figure 5c. The rapid decrease in $Q_{cha}$ ($Q_{dis}$) during the initial five cycles was also reported for previous $\beta$-FeOOH compounds. To reveal the origin of the capacity fading, discharge and charge tests at a low current (0.1 mA) were conducted for HP(400 °C). As indicated by the blue lines in Figure 5b, the $Q_{cha}$ value recovered to $481.5$ mA h$^{-1}$ at 0.1 mA, suggesting that the capacity fading in HP(400 °C) originates from a kinetic factor such as the isolation of $\epsilon$-FeOOH from the conductive carbon. Note that the $Q_{dis}$ value at 0.1 mA was limited to $332.9$ mA h$^{-1}$. This finding indicates that the charge reaction is slower than the discharge reaction, and thus, Li$^+$ ions remain in the $\epsilon$-FeOOH particles in the charge-end state. Further optimizing the particle size and electrode mixture could improve the cyclability of $\epsilon$-FeOOH.

Ex situ XRD measurements were performed on HP(400 °C) to clarify the stability of $\epsilon$-FeOOH during the discharge reaction. Figure S6 shows the XRD patterns at discharged states of 1.2 V (D1), 1.0 V (D2), and 0.02 V (D3). The diffraction lines originated from the $\epsilon$-FeOOH phase almost disappeared at D1, and three weak diffraction lines were observed at 2θ = 54.71, 81.21, and 105.54 °. The XRD pattern at D2 was similar to that at D1, but the intensities of the three diffraction lines became weak at D3. Although it is currently difficult to assign the above three diffraction lines, the cubic lattice parameter ($a_\epsilon$) was estimated to be 4.205(1) Å assuming for a rock-salt (LiFe)O phase. This lattice parameter is comparable to $a_\alpha$ (4.162 Å) of $\alpha$-LiFeO$_2$ with a rock-salt structure.42

We then investigated the performance of $\epsilon$-FeOOH as a negative electrode material for NIBs because $\beta$-FeOOH exhibited a $Q_{cha}$ of $\sim$500 mA h g$^{-1}$. Figure 6a shows the discharge and charge curves of a Na cell with the HP(400 °C) sample operated at a current of 0.1 mA and 25 °C. (b) Corresponding $dQ_{dis}/dV$ (or $dQ_{cha}/dV$) curve at the first cycle.

CONCLUSIONS

An almost single phase of $\epsilon$-FeOOH was synthesized from $\alpha$-FeOOH using the HP/HT method and examined in nonaqueous Li and Na cells. The primary particles of the $\epsilon$-FeOOH sample synthesized at 500 °C indicated a plate-like
morphology with a thickness of ~200 nm and a lateral length of ~1 μm. This particle morphology was significantly different from that of α-FeOOH, in which secondary particles were formed by needle-shaped primary particles with dimensions of ~100 × 500 nm. The ε-FeOOH/Li cell exhibited a Q_{cha} of 700 mA h g⁻¹ at 0.02–3.0 V, which was similar to that of α-FeOOH. However, the Q_{cha} of the α-FeOOH/Li cell rapidly decreased to ~340 mA h g⁻¹ with the increasing applied current (0.3 mA). The Q_{cha} values of ε-FeOOH at the charge currents of 0.6, 1.0, and 2.0 mA were greater than those of α-FeOOH. Hence, ε-FeOOH was found to provide a better rate capability than α-FeOOH. Furthermore, because the δ_{XRD} of ε-FeOOH is the highest among the FeOOH polymorphs, ε-FeOOH enables increasing the volumetric energy density of LIBs. Unfortunately, a Q_{cha} of less than 30 mA h g⁻¹ was observed in the ε-FeOOH/Na cell, in contrast to cells with β-FeOOH. The particle size and electrode mixture should be further optimized to improve the cyclability of ε-FeOOH.

■ EXPERIMENTAL SECTION

Sample Preparation. First, ε-FeOOH was synthesized using the HP/HT method using the Walker-type equipment at the Osaka Prefecture University, as previously reported.39,40,46,47 Approximately 50 mg of α-FeOOH powder (Koujyundo Chemical Laboratory Co., Ltd.) was packed into a (MgCo)O pressure medium (Mino Ceramics, Ltd.) and then placed at the center consisting of tungsten carbide anvils with eight truncations (Fuji Die Co., Ltd.). After reaching a pressure of 8 GPa, each sample was heated at 100, 200, 300, 400, 500, 600, 700, or 800 °C for 30 min.

Characterization. The obtained samples were characterized via SEM (S-3600 N, Hitachi High-Technologies) and XRD measurements using a Fe Kα radiation source (D8 ADVANCE, Bruker AXS). Before SEM observations, approximately 1 mg of sample, which was attached onto the sample holder with a carbon tape, was coated with electrically conducting Au particles (IB-3, Eiko Co., Ltd.). We also employed a field-emission SEM system (SU8020, Hitachi High-Technologies) for several samples. For this observation, samples were coated with Os particles (HPC-1S, Vacuum Device Inc.). Rietveld analyses were conducted using RIETAN-FP software,48 and the crystal structures were drawn using VESTA software.49 TG/differential thermal analysis was conducted in air up to 1000 °C at a heating rate of 20 °C min⁻¹.

Electrochemical Measurements. Discharge and charge curves were recorded using the nonaqueous Li and Na cells. For the Li and Na cells, the electrolytes were 1 M LiPF₆ and 1 M NaPF₆ separately dissolved in ethylene carbonate (EC)/ diethylene carbonate (DEC) (EC/DEC = 1/1 by volume, Kishida Chemical Co., Ltd.), respectively. For both types of cells, a mixed electrode consisting of 70 wt % active material, 20 wt % conducting carbon (acetylene black, AB, HS-100, Denka Co., Ltd.), and 10 wt % PTFE (Daikin Industries, Ltd.) was used as the working electrode (diameter = 10 mm), while Li or Na metal pressed onto a stainless steel plate (diameter = 19 mm) was used as the counter electrode. After being fabricated in an argon-filled glovebox, the Li cells were operated at a current of 0.1 mA, while the Na cell was operated at a current of 0.3 mA. The rate capability test was performed only for the Li cells at the charge currents of 0.3, 0.6, 1.0, and 2.0 mA. The discharge current was fixed to 0.1 mA. The current of 0.1 mA corresponds to a current density of ~0.1 mA cm⁻². The voltage ranges were 0.02–3.0 or 1.0–3.0 V for the Li cells and 0.02–2.7 V for the Na cell. The environmental temperature of the cells was 25 °C.

Ex Situ XRD Measurements. We performed ex situ XRD measurements on HP(400 °C) to clarify the stability of ε-FeOOH. Three lithium cells were fabricated using the 1 M LiPF₆/EC + DEC electrolyte, and then each lithium cell was discharged to 1.2 (D1), 1.0 (D2), or 0.02 (D3) V at a current of 0.1 mA. The discharge curves are shown in Figure 6a. The mixed electrode containing AB and PTFE was removed in an argon-filled glovebox and covered with a Kapton tape to avoid reactions with a moist air. Open-circuit voltages just before the ex situ XRD measurements were 1.771 V for D1, 1.573 V for D2, and 0.360 V for D3. XRD patterns were recorded using the Fe Kα radiation source.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00728.

Rietveld analysis results and structural parameters of the pristine α-FeOOH sample; Rietveld analysis results of HP(400 °C) and HP(500 °C); TG curve of HP(500 °C) discharge and charge curves at 1.0–3.0 V of α-FeOOH, HP(400 °C), and HP(800 °C); rate capability of HP(300 °C) (α-FeOOH) and HP(400 °C) (ε-FeOOH); and ex situ XRD patterns at several discharged states (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors wish to thank Dr. Takeshi Morikawa, Dr. Tomiko M. Suzuki, and Takeshi Uyama of TCRDL for discussions about FeOOH polymorphs and their potential applications.

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