Hydrothermal synthesis and electrochemical properties of FeNbO₄ nanospheres

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Iron niobate (FeNbO₄) nanospheres of an orthorhombic structure were synthesized using a hydrothermal (HT) process at 250°C, and were characterized using X-ray diffraction, field-emission scanning electron microscopy, high-resolution transmission electron microscopy, and Brunauer–Emmett–Teller (BET) measurements. The FeNbO₄ nanospheres obtained through the HT reaction revealed a uniform size with an average diameter of 5–10 nm, and a larger specific surface area (82.72 m² g^{−1}) than that of bulk FeNbO₄ powder (2.51 m² g^{−1}) prepared by a solid-state reaction. In addition, the electrochemical properties of the FeNbO₄ powders versus Li were evaluated using cyclic voltammetry and galvanostatic charge/discharge cycling. Importantly, the FeNbO₄ nanospheres delivered a reversible capacity of over 200 mAh g^{−1} after 20 cycles, and provided an enhanced rate capability compared to the bulk material.

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1. Introduction

Nanomaterials have been widely applied in the life sciences, the environment, information technology, and other related fields. Recently, inorganic nanostructures such as nanospheres, nanowires, nanorods, and nanosheets have also triggered a great deal of interest in terms of their application in energy-storage devices.^{1),2)} Of the many energy-storage devices available, Li-ion batteries have been studied most intensively with a variety of nanostructured inorganic materials. In particular, most of the nanostructured materials explored as electrode materials for Li-ion batteries provided enhanced electrochemical performances compared to the bulk materials because of the high reactivity associated with their porosity, extremely high surface area, and so on. Furthermore, the high reactivity found at the nanolevel can open the possibility of finding new and novel Li insertion hosts.

In this context, some types of nanostructured ABO₄ oxides, e.g., FeNbO₄, FeTaO₄, and AlNbO₄, can be an attractive group as electrode materials for Li-ion batteries because of their open crystal structures, indicating favorable Li intercalation/deintercalation. However, in spite of a fabrication of nanostructured ABO₄ materials using various synthesis methods, most of them have been investigated only as gas sensors or photo anode materials until now.^{3)–6)} In particular, in the case of FeNbO₄, the magnetic and photocatalytic properties with a variety of synthetic methods have been studied.^{7),8)} More recently, our group has reported the synthesis of FeNbO₄ nanoparticles using hydrothermal process and have achieved enhanced photocatalytic activity, compared to FeNbO₄ prepared by a conventional solid-state reaction at 1000°C.⁹⁾ Although a few reports have illustrated the use of such materials for Li-ion battery electrodes, to the best of the authors' knowledge, there has been no report on the use of FeNbO₄ as a Li-ion battery anode material.

Herein, we report the synthesis of iron niobate (FeNbO₄) nanospheres with an orthorhombic structure, prepared through a simple hydrothermal process to reduce the particle size, and present their first application as a Li-ion battery anode. Furthermore, compared to the electrochemical performance of as-synthesized bulk FeNbO₄ powder, which was prepared through the conventional solid-state reaction and annealing process, the FeNbO₄ nanospheres were demonstrated to have superior electrochemical characteristics.

2. Experimental details

The preparation of FeNbO₄ powders was carried out by: (i) a solid-state (SS) reaction; and (ii) a hydrothermal (HT) method.⁹⁾ In the case of the SS method, mixtures composed of commercial α -Fe₂O₃ and Nb₂O₅ were used as the starting materials; they were weighed in appropriate stoichiometric ratios, homogenized well by ball-milling with zirconia media for 24 h, and then calcined in air at 1200°C for 2 h. For the HT method, a 15 mM aqueous solution of each of the starting materials [Fe(NO₃)₂·6H₂O and NbCl₅] was prepared by dissolving the materials in 100 mL of distilled water and absolute ethanol (99.9%), respectively, under constant magnetic stirring. Then, equal volumes (100 mL) of these solutions were mixed. Before the HT reaction, the mixed solutions were adjusted to pH 10.0 using NH₄OH solution and stirred for 30 min. Finally, it was transferred into a Teflon-lined autoclave, and the reaction was allowed to proceed for 24 h at 250°C. After the HT reaction, the reddish-brown precipitate was collected by centrifugation and washed with distilled water and absolute ethanol. Subsequently, the precipitate was dried at 90°C in an oven.

The microstructures and phase identities were determined using a field-emission scanning electron microscope (FESEM, model JSM-6330F, JEOL Co., Japan), an X-ray powder diffractometer (XRD, model M18XHF-SRA, Mac Science Co., Japan), and a transmission electron microscope (TEM, model

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JEM-2100F, JEOL Co., Japan) at an accelerating voltage of 200 kV. High-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) pattern were investigated for further sample analysis. In addition, the specific surface area of the as-prepared samples was measured using Brunauer–Emmett–Teller (BET) surface-area analyzer (model ASAP 2010, Micromeritics Instrument Co., USA).

The fabrication of the FeNbO_4 electrodes was conducted by mixing the active material (FeNbO_4 powder, 1–2 mg), Super P carbon black (MMM Carbon, Brussels, Belgium), and Kynar 2801 binder in a mass ratio of 70:15:15 in 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich). After adequate mixing, the slurry mixture was coated onto Cu foil and dried in a vacuum oven at 100°C for 6 h, and then the electrodes were pressed and cut.

The electrochemical performances of the as-prepared FeNbO_4 electrodes as anodes were estimated using Swagelok™-type half cells (FeNbO_4 electrode/Li metal foil), in which a Li metal foil electrode was used as the counter electrode. The cells were assembled in an Ar-filled glove box using the electrodes, a separator film of Celgard 2400, and an electrolyte. The electrolyte was 1 M LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of EC/DMC = 1:1 (TechnoSemichem, Korea).

The fabricated cells were cycled galvanostatically at a current rate of C/5, and the results were recorded in the voltage window between 0.01 and 3.0 V by means of a multichannel potentiostatic/galvanostatic system (model WBCS 3000, WonATech Co., Korea).

3. Results and discussion

Figure 1(a) shows typical FESEM image of the as-prepared FeNbO_4 nanospheres. It is clearly seen that the FeNbO_4 nanospheres (hereafter HT-FNO) could be synthesized directly through a facile HT crystallization process. The obtained nanospheres

Fig. 1. (Color online) (a) Typical FESEM image of FeNbO_4 nanospheres, (b) X-ray diffraction patterns of FeNbO_4 nanospheres that correspond with the orthorhombic-structure.

exhibited a uniform size distribution with an average diameter of 10–80 nm, which is assembled by small particles. For comparison, we also prepared bulk FeNbO_4 powder using the conventional solid-state method at 1200°C. Obviously, the bulk FeNbO_4 powder (hereafter SS-FNO) revealed a denser microstructure as well as a much larger particle size and agglomeration than the HT-FNO. These results were also confirmed by BET surface-area analysis. As expected, in the case of HT-FNO, the specific surface area was $82.72 \text{ m}^2 \text{ g}^{-1}$, whereas that of SS-FNO was $2.51 \text{ m}^2 \text{ g}^{-1}$. Obviously, this meant that the particle size and degree of aggregation in FeNbO_4 was remarkably reduced when the HT method was employed. The crystal structures of the obtained HT-FNO powders were determined through the analysis of XRD patterns, as shown in Fig. 1(b). For the amorphous powders hydrothermally prepared at 180°C for 12 h, post-heat-treatment (600–800°C) should be needed to obtain the crystalline phase of FeNbO_4 .⁹⁾ By increasing the hydrothermal temperature and time, the crystalline FeNbO_4 powders were successfully formed without post-heat-treatment. All the reflection peaks of the as-prepared HT-FNO powders by a hydrothermal process at 250°C for 24 h were appropriately indexed as a crystalline, orthorhombic structure, and were in good agreement with the literature values (JCPDS file No.: 84-1981, space group: *Pbcn*) for FeNbO_4 .

The morphological characteristics of HT-FNO were further investigated using HRTEM, as shown in Fig. 2. The representative overview images of the HT-FNO observed in Figs. 2(a) (low-magnification) and 2(b) (high-magnification) illustrate that the sizes of the nanoparticles were in the range 5–10 nm; these were consistent with the observed FESEM results. Moreover, the indexed SAED pattern indicated the single-crystal nature of the nanospheres in the orthorhombic structure, as shown in Fig. 2(c). In addition, the HRTEM image [Fig. 2(d)] of the nanospheres, which was taken from the open square region in Fig. 2(b), also shows that the nanospheres were structurally uniform, with interplanar spacings of about 0.293 and 0.278 nm, corresponding to the lattice spacings of the (111) and (020) planes of the orthorhombic FeNbO_4 structure, respectively. Furthermore, from

Fig. 2. (Color online) Representative TEM images of FeNbO_4 nanospheres. (a) Low- and (b) high-magnification, (c) SAED pattern, (d) the HRTEM image in the open-square region of (b).

Fig. 3. (Color online) Cyclic voltammetry profiles of FeNbO₄ nanospheres in the first three cycles. Inset is crystal structure view of FeNbO₄ in a-b plane.

the HRTEM image in Fig. 2(d), we could confirm that an individual HT-FNO nanoparticle was approximately 7 nm in diameter. It exhibited clearly distinguishable grain boundaries with high crystallinity, even though the nanoparticles were slightly aggregated.

Figure 3 shows the CV profile of the HT-FNO electrode during the first three cycles performed between 0.01 and 3.0 V (vs. Li⁺/Li) at a scan rate of 0.3 mV s⁻¹. The first sweep commenced cathodically from the open-circuit voltage (OCV). The first cathodic peaks occurred at ≈0.64 and ≈0.53 V. The subsequent charge cycles indicated anodic peaks at ≈1.04 and ≈2.01 V. However, the following cycles showed a pair of redox peaks at ≈1.10 and ≈0.67 V in the discharge cycle and at ≈0.97 and ≈1.90 V in the charge cycle. These peaks could not correspond to the Nb⁵⁺/Nb⁴⁺ redox couple located near 1.6 and 1.7 V, which was reported in the CV curves of other Nb-based material, KNb₅O₁₃.¹⁰⁾ In addition, the cathodic peak by the reduction process of Fe³⁺ to Fe⁰ should be observed at ≈0.8 V.¹¹⁾ It is not clear whether the valence variations of both Nb⁵⁺/Nb⁴⁺ and Fe³⁺/Fe²⁺ redox couples were fully achieved or the electronic structure of the FeNbO₄ were changed by the insertion of Li ions. Further in-situ X-ray absorption spectroscopy measurements are needed in order to clarify the total reduction of each metal at preset voltage states.

Figure 3 inset shows the crystal structure view of FeNbO₄ with the orthorhombic structure in the a-b plane. The structure is based upon the zigzag chain-stacking sequence, such as an ABAB stacking sequence (where A and B are FeO₆ and NbO₆ octahedra chains, respectively) of closest packing of oxygen atoms, where one quarter of the octahedral voids are occupied by metal ions and each metal ion is randomly distributed on one crystallographic site. Overall, this FeNbO₄ framework contains a-b slabs of edge-sharing (Fe,Nb)O₆ octahedra chains (zigzag chains), arranged to create periodic corner-sharing c-axis connections between neighboring slabs that give strong 3D bonding. The corner-sharing octahedra are separated by octahedra sharing only edges; this creates perpendicular intersecting 1D tunnels in the [001] direction, parallel to the a and b axes in the a-b plane of the orthorhombic structure. Importantly, these 1D channels can serve as a pathway for favorable intercalation/deintercalation upon transfer of Li ions.

Figure 4 shows the typical charge/discharge curves of the as-prepared HT-FNO electrode. The curves were recorded at a current rate of 74.4 mA g⁻¹ for 20 cycles, at room temperature,

Fig. 4. (Color online) Plot of charging-discharging curves of FeNbO₄ nanospheres electrode in the voltage range of 0.01–3.0 V at a current rate of C/5. Inset shows a comparison of rate capabilities of all FeNbO₄ electrodes at different current rates.

for a potential window between 3.0 and 0.01 V (vs. Li⁺/Li). As shown in Fig. 4, there was a narrow potential plateau at ≈1.0 and 0.64 V (vs. Li⁺/Li) in the first discharge cycle, for which the discharging plateau corresponded with the cathodic peak of the CV profile. After the first cycle, the potential gradually decreased to 0.01 V possibly because of kinetic limitations.¹²⁾ Upon subsequent galvanostatic oxidation, the charge curve showed a steady voltage increase, but a weak charge-potential plateau was observed at around 1.0 and 2.0 V (vs. Li⁺/Li), which was related to the oxidation peak in the CV, as shown in Fig. 3. Although these potential plateaus are narrow and indistinguishable from the charge/discharge curves, it is thought that distinct plateaus on both the charge and discharge curves can be observed at the voltages induced by the redox reaction through the relatively low current rate.

After the first discharge process, we observed a high specific capacity of around 1000 mAh g⁻¹. This higher specific capacity can be attributed to the formation of a Li-bearing solid-electrolyte-interface (SEI) layer, similar to the one forming on carbon electrodes.^{13),14)} Importantly, the reversible specific capacity of HT-FNO exhibited a high value of over 200 mAh g⁻¹ after 20 cycles. More importantly, as depicted in inset of Fig. 4, the electrochemical performance in terms of the rate capability of the HT-FNO was evaluated and compared with that of the SS-FNO. The cells were first cycled at a rate of 37.2 mA g⁻¹, and after every 10 cycles the rate was increased to 186.0 mA g⁻¹. As expected, the HT-FNO clearly exhibited a better specific capacity at different current rates, indicating enhanced rate capability, than the corresponding capacities achieved under identical conditions for the SS-FNO. With the value measured at rates of 37.2, 74.4, 124.0, and 186.0 mA g⁻¹, all FeNbO₄ electrodes delivered the specific capacities of 288, 188, 146, and 106 mAh g⁻¹ in the HT-FNO and 152, 108, 89, and 74 mAh g⁻¹ in the SS-FNO, respectively. These results can be explained to the extremely large surface area of the HT-FNO, originating from their low-dimensionality and degree of aggregation, as depicted in FESEM and TEM images [Fig. 1(a) and Fig. 2].

As mentioned, due to the extremely high surface area, the nanostructured materials can provide shorter path length for both Li-ion and electron transport and a higher electrode/electrolyte contact area, and therefore it can lead to improved high current rate charge/discharge capacities with good cycle stability and

rate capability. In this work, the BET surface area of between the HT-FNO and SS-FNO indicated tremendous difference over forty times, including 82.72 and 2.51 m² g⁻¹, respectively, with obviously distinct agglomeration. As results of those effects, the HT-FNO can lead to enhanced Li-storage properties as well as good rate capability, compared to the SS-FNO. Furthermore, the electrical conductivity of FeNbO₄ has been reported to be a relatively poor value, $2.5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at room temperature.¹⁵⁾ Therefore, the surface modification using conductive carbon could possibly improve the electrochemical performance of the HT-FNO electrodes.

4. Conclusions

In summary, FeNbO₄ nanospheres of the orthorhombic structure were synthesized using a facile HT process, and their lithium electroactivities were investigated for the first time. Compared to bulk FeNbO₄ powder prepared through a conventional solid-state reaction method, the obtained nanospheres exhibited a smaller and more uniform size, averaging 5–10 nm in diameter. More importantly, the FeNbO₄ nanospheres had a much larger specific surface area (around 83 m² g⁻¹) than their bulk counterpart (2.5 m² g⁻¹). In particular, this larger surface area, resulting from the reduced dimensionality, led to an enhanced rate capability as well as a high reversible capacity of over 200 mAh g⁻¹ after 20 cycles at a current rate of 74.4 mA g⁻¹, and to a coulombic efficiency exceeding 95%.

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