Hydrothermal-Assisted Sintering Strategy Towards Porous- and Hollow-Structured LiNb₃O₈ Anode Material

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Abstract

Porous- and hollow-structured LiNb₃O₈ anode material was prepared by a hydrothermal-assisted sintering strategy for the first time. The phase evolution was studied, and the formation mechanism of the porous and hollow structure was proposed. The formation of the unique structure can be attributed to the local existence of liquid phase because of the volatilization of Li element. As the anode material, the initial discharge capacity is 285.1 mAhg⁻¹ at 0.1 C, the largest discharge capacity reported so far for LiNb₃O₈. Even after 50 cycles, the reversible capacity can still maintain 77.6 mAhg⁻¹ at 0.1 C, about 2.5 times of that of LiNb₂O₅ samples prepared by traditional solid-state methods. The significant improvement of Li storage capacity can be attributed to the special porous and hollow structure, which provides a high density of active sites and short parallel channels for fast intercalation of Li⁺ ions through the surface.

Keywords: LiNb₃O₈, Anode, Lithium-ion batteries, Porous and hollow structure

Background

In recent years, much attention has been paid to hollow and porous structures due to their widespread applications in catalysis, energy, environmental engineering, drug delivery, and sensor systems [1–4]. Compared with other new energy batteries, lithium-ion batteries (LIBs) have gained commercial success as the predominant power source for portable electronics and show great potential in large-scale applications because of its high energy density, long lifespan, and environmental benignity [5]. To obtain high electrochemical performance, the electrodes of LIBs always have open structures, which can provide a high density of active sites and parallel channels for faster intercalation of Li⁺ ions through the surface [6]. However, it is challenging to synthesize the nanomaterials with open structures including porous and hollow architectures.

To improve LIBs performances, people have been seeking for high-performance electrode materials, including anode and cathode materials. LiFePO₄ [7], LiCoO₂ [8], LiMn₂O₄ [9], LiVPO₄F [10], and various hybrid materials [11, 12] have been seriously considered as candidates for cathode materials. For anode materials, many different materials have been investigated as alternatives to graphite-based anode materials, such as transition metal oxides (TMOs) [13], molybdenum disulfide (MoS₂), and graphene-based hybrids [14]. In recent literature, niobium has been shown to have superior electrochemical performance [15]; some traditional compounds doped with Nb element and novel Nb-based compounds are well developed [16–19]. Nb-based oxides have been considered as promising anode materials for LIBs with improved safety. Compared with Li₄Ti₅O₁₂ (with a theoretical capacity of 175 mAhg⁻¹), Nb-based oxides have a relatively high theoretical capacity of 389 mAhg⁻¹. Also, it is notable that the two Nb redox couples, Nb⁵⁺/Nb⁴⁺ and Nb⁴⁺/Nb³⁺, can suppress the formation of solid electrolyte interface (SEI) film during cycling [19]. LiNb₃O₈, a well-known material, always appear in the preparation process of LiNbO₃ as an impurity phase due to Li volatilization [20]. Jian et al. firstly

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introduced LiNb₃O₈ material prepared by a solid-state reaction as an anode for LIBs. It is found that the as-prepared LiNb₃O₈ sample ball-milled with acetylene black (LiNb₃O₈-BM) largely improved the initial discharge/charge capacities (351 and 212 mAh g⁻¹) than those of the as-prepared LiNb₃O₈ sample (250 and 170 mAh g⁻¹) at 0.05 C; after 50 cycles, the capacity reached 150 mAh g⁻¹ for LiNb₃O₈-BM at 0.1 C, only 30 mAh g⁻¹ for LiNb₃O₈ sample [18]. Porous LiNb₃O₈ nanofibers also exhibited improved capacity and cyclability in virtue of the high surface area, small nanocrystals, and porous structure with the initial discharge capacity of 241.1 mAh g⁻¹ at 0.1 C [19]. Due to the difficulty to obtain pure phase, as a novel anode material with high theoretical capacity, LiNb₃O₈ has rarely been studied.

In this paper, porous- and hollow-structured LiNb₃O₈ anode material was successfully prepared by a hydrothermal-assisted sintering process. The phase evolution was studied, and the formation mechanism of the porous and hollow structure was proposed. The morphological and electrochemical properties of LiNb₃O₈ as the anode material were also studied in detail.

Methods

Preparation of Samples

LiNb₃O₈ powders were prepared by the hydrothermal-assisted sintering process. Lithium hydroxide monohydrate (LiOH·H₂O, Aladdin, ACS, ≥98.0%) and niobium pentoxide (Nb₂O₅, Aladdin, AR, 99.9%) were purchased as raw materials without further purification. First, 3.5 mmol of Nb₂O₅ was dispersed into 35 ml of LiOH·H₂O transparent aqueous solution (the mole ratio of Li:Nb = 8:1) with magnetic stirring for 1 h. Then, the suspension solution was put into a 50-ml Teflon-lined hydrothermal synthesis autoclave reactor. After that, the reactor was sealed and maintained at 260 °C for 24 h and then cooled down to room temperature naturally. Finally, the as-prepared products were centrifuged and rinsed with deionized water and ethanol. After drying in an oven at 60 °C for 12 h, the white Li-Nb-O powders were collected and calcined at various temperatures from 500 to 800 °C for 2 h with a ramp rate of 5 °C/min.

Characterization

The thermal decomposition characteristic of Li-Nb-O powder was studied by a thermogravimetric and differential scanning calorimeter (TG/DSC, Netzsch STA 409 PC/PG) from room temperature to 1200 °C with a ramp rate of 10 °C/min under N₂ atmosphere. The crystal structures of the calcined powders were analyzed using X-ray powder diffraction (XRD; Bruker D8 Discover) with Cu Kα radiation. The morphologies of the calcined powders were characterized by scanning electron microscopy (SEM; JSM-6700F). X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo-Fisher Escalab 250Xi instrument.

Electrochemical Measurements

The LiNb₃O₈ electrodes were prepared by spreading slurry of LiNb₃O₈ powders, carbon black, and poly(vinylidene fluoride) (PVDF) with a weight ratio of 8:1:1 onto an aluminum foil. Afterward, the electrode was dried at 120 °C in a vacuum oven overnight. The anodes were punched into disks with a diameter of 16 mm. For the electrochemical measurements, CR2025 coin-type cells were assembled in an argon-filled glove box using lithium foil as the counter electrode and polypropylene microporous membrane (Celgard 2320) as a separator to isolate the two electrodes, and then, the 1.0-M LiPF₆ electrolyte was dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 by volume). Galvanostatic charge-discharge tests of the cells were performed using a Land electric test system (Wuhan Land Electronics Co., Ltd., China) between 0 and 3 V (vs. Li/Li⁺) at different current densities of 0.1–1 C (1 C = 389 mAh g⁻¹). Cyclic voltammetry (CV) curves were recorded on an electrochemical workstation (CHI604E, Shanghai Chenhua Instruments Co., Ltd., China) in the voltage range of 1−3 V.

Results and Discussion

Figure 1 plots the TG/DSC curves of the powder obtained after hydrothermal reaction without further calcination. The weight loss of the powder is very small, about 5%, even as the temperature reaches to 1100 °C, but the loss is occurring throughout the entire calcination process. This can be attributed to the evaporation of Li element due to its low melting temperature, which is confirmed by the DSC results with endothermic reaction process throughout the entire calcination process. At 330 °C, an endothermic peak occurs, which may
originate from the formation of LiNbO$_3$. An exothermic reaction occurs at 580 °C resulting from the reaction between LiNbO$_3$ and Nb$_2$O$_5$ to form LiNb$_3$O$_8$. As seen in the DSC curve, beyond 1100 °C, the exothermic reaction becomes strong due to the decomposition of LiNb$_3$O$_8$.

The XRD patterns of Li-Nb-O powders calcined at different temperatures are shown in Fig. 2. It can be seen that the major phases are LiNbO$_3$ and Nb$_2$O$_5$ at 500 °C. With the increase of calcination temperature, the diffraction peak at 30.26° appears which can be indexed as the (410) plane of monoclinic LiNb$_3$O$_8$. The reaction can be described by Eq. (1) not Eq. (2) [21]:

\[
\text{LiNbO}_3 + \text{Nb}_2\text{O}_5 \rightarrow \text{LiNb}_3\text{O}_8
\]

\[
\text{LiNbO}_3 \rightarrow \text{LiNb}_3\text{O}_8 + \text{Li}_2\text{O}↑
\]

At 700 °C, the monoclinic LiNb$_3$O$_8$ is the predominant phase with almost negligible impurity. The pure phase of LiNb$_3$O$_8$ is obtained at 800 °C with all the diffraction peaks indexed to the monoclinic phase (JCPDS card no. 36–0307), a space group of P21/a. Compared with the traditional solid-state method, the pure phase of LiNb$_3$O$_8$ is more easily obtained using the hydrothermal-assisted sintering process.

The SEM images of LiNb$_3$O$_8$ powder calcined at 800 °C with different magnifications are presented in Fig. 3. The porous and hollow structure that resembles a honeycomb is formed by LiNb$_3$O$_8$ nanoparticles with the length of several micrometers. The structure is not flat, with obvious warping, and even forms closed tubby-like structures. It is fully different from the particle aggregation that results from conventional solid-state reactions. The size of the LiNb$_3$O$_8$ particle is about 200 nm, as shown in Fig. 3c. The small particle size and unique structure are beneficial to ion intercalation [6]. The formation of the unique structure can be attributed to the lithium volatilization during the calcination process, as proved by TG-DSC results. As the easy volatilization of Li element, the excess Li element existing in the powder easily migrates to the surface of particles and turns into liquid phase. The local existence of liquid phase is conducive to the formation of new LiNb$_3$O$_8$ particles at the site and also encourages the formation of networks between the particles.

To further confirm the elemental compositions and the electronic state, the porous- and hollow-structured LiNb$_3$O$_8$ powders are analyzed by XPS, as shown in Fig. 4. The XPS data were calibrated using C 1s as a reference with the binding energy at 284.6 eV. In Fig. 4a, two peaks at 207.1 and 209.8 eV correspond to Nb 3d$_{5/2}$ and 3d$_{3/2}$, respectively, indicating the Nb$^{5+}$ state in LiNb$_3$O$_8$ [22]. The XPS spectra of O 1s in Fig. 4b can be deconvoluted into two peaks at 530.3 and 532 eV. The former is assigned to the Nb-O bonds, and the latter is related to nonlattice oxygen [22, 23].

To investigate the electrochemical performance of the as-prepared LiNb$_3$O$_8$ sample, the tests of CV and galvanostatic discharge-charge cycling were performed. The first three CV curves of LiNb$_3$O$_8$ powder at a scanning rate of 0.1 mV/s in the range of 3~1 V are shown in Fig. 5. In the first cycle, two pronounced peaks (Li insertion) are observed at 1.13 and 1.30 V; the former can be attributed to the partial reduction of Nb$^{4+}$ to Nb$^{3+}$, while the latter can be related to the full valence variation of Nb$^{5+}$ to Nb$^{4+}$ [18, 19]. As seen in Fig. 5, the subsequent cycles are quite different from the first cycle. The disappearance of the peaks at 1.13 and 1.30 V implies the phase transition in the first cycle is irreversible. Only the oxidation (Li extraction) peaks at 1.71 and 1.96 V remain stable upon cycling, implying the structure change of the LiNb$_3$O$_8$ sample in subsequent cycles is reversible.

Figure 6 shows the discharge-charge curves of the LiNb$_3$O$_8$ powder at 0.1 C (here, 1 C = 389 mAh g$^{-1}$) between 3 and 1 V in the first, second, tenth, thirtieth, and fiftieth cycles. In the first discharge curve, two obvious potential plateaus can be observed at approximately 1.13 and 1.30 V, which is in good agreement with the CV results that two phase reactions, Nb$^{4+}$ $\rightarrow$ Nb$^{3+}$ and Nb$^{5+}$ $\rightarrow$ Nb$^{4+}$, take place. However, in the subsequent cycles, the plateaus that exist in the first cycle are replaced by sloping curves, implying different reactions between the first and subsequent cycles. At the same time, the initial discharge capacity of the LiNb$_3$O$_8$ sample is 285.1 mAh g$^{-1}$ at 0.1 C, the largest discharge capacity reported so far for LiNb$_3$O$_8$ anode materials [18, 19]. 4.4 Li per unit formula can be inserted into the LiNb$_3$O$_8$ material, corresponding to a composition of Li$_{5.4}$Nb$_3$O$_8$. However, the charge capacity in the first cycle is 106.4 mAh g$^{-1}$, indicating that...
only 1.6 Li can be extracted reversibly. The big loss of 2.8 Li is ambiguous at present.

Figure 7 shows the cycling performance of LiNb$_3$O$_8$ sample at different current rates up to 50 cycles. The initial discharge capacities of LiNb$_3$O$_8$ powder at rates of 0.1, 0.5, and 1 C are 285.1, 250, and 228 mAh g$^{-1}$, respectively. At a current rate of 0.1 C, the reversible capacity can still maintain 77.6 mAh g$^{-1}$, about 2.5 times of that of LiNb$_3$O$_8$ samples prepared by traditional solid-state method (about 30 mAh g$^{-1}$ at 0.1 C, Ref. [18]). The significant improvement of Li storage capacity can be attributed to the special porous and hollow structure of LiNb$_3$O$_8$ sample, which provides a high density of active sites and short parallel channels for faster intercalation.

![Fig. 3](image1) SEM images of LiNb$_3$O$_8$ powder with different magnifications

![Fig. 4](image2) XPS spectra of (a) Nb 3d and (b) O 1s for the porous- and hollow structured LiNb3O8

![Fig. 5](image3) The initial three CV curves of the LiNb$_3$O$_8$ powder at a scan rate of 0.05 mV/s between the voltage ranges of 3–1 V.
of Li$^+$ ions through the surface [6]. When the rates increase to 0.5 and 1 C, the discharge capacities after 50 cycles remain 39.7 and 29.4 mAhg$^{-1}$, respectively. It is expected that the capacity stability can be improved by suitable surface modification on LiNb$_3$O$_8$ material.

Conclusions

In summary, porous- and hollow-structured LiNb$_3$O$_8$ anode material was successfully prepared by the hydrothermal-assisted sintering strategy. The phase evolution was studied, and the formation mechanism of the porous and hollow structure was proposed. The formation of the unique structure can be attributed to the local existence of liquid phase because of the Li volatilization. As the anode material, the initial discharge capacity is 285.1 mAhg$^{-1}$ at 0.1 C, the largest discharge capacity reported so far for LiNb$_3$O$_8$. After 50 cycles, the reversible capacity can still maintain 77.6 mAhg$^{-1}$, about 2.5 times of that of the LiNb$_3$O$_8$ samples prepared by traditional solid-state methods. The significant improvement of Li storage capacity can be attributed to the special porous and hollow structure of LiNb$_3$O$_8$ powder, which provides a high density of active sites and short parallel channels for fast intercalation of Li$^+$ ions through the surface.

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Authors’ Contributions

HZ carried out the main part of the experimental work and XRD measurements. HLiu performed the XPS tests. HLZ, LZ, and XZ participated in the preparation of the samples. CH performed the SEM images measurements. QL and JY carried out the electrochemical measurements and participated in the analysis of the data. All authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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