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Research on Niobate Anode Materials

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Abstract

Niobate has become an advanced anode material that can be used in lithium-ion batteries due to its higher voltage and the presence of multiple single-electron redox pairs relative to lithium, which will result in higher capacity and better safety. However, because of the electron distribution of the internal elements, it causes problems such as low conductivity. Therefore, at this stage, researchers have been carried out to solve this problem. This paper takes $TiNb_xO_{2.5x+2}$ (x=2, 10 or 14) anode material as the main object of discussion, and discusses the application of $TiNb_xO_{2.5x+2}$ in lithium-ion batteries as well as the modification strategy.

Keywords

Niobates; Lithium-ion Batteries; Anode Materials; Modification; Crystal Structure.

1. Introduction

In order to reduce the consumption of fossil energy in nature and to build a better ecological civilization, people have started to look for new energy sources that can produce the same or even better energy to replace the consumption of non-renewable energy sources. Wind and solar energy are affected by geographic factors, so it is particularly important to utilize these materials or to better store this type of energy.

At this stage, energy storage products continue to develop, and lithium-ion batteries have been widely used in transportation and wearable devices at this stage due to their high energy density, long sustainable use time, and the fact that they do not produce toxic and hazardous substances in the process of use.[1] Lithium-ion batteries are mainly composed of positive electrode, negative electrode, diaphragm and electrolyte, and the storage performance of electrical energy depends largely on the processing performance of electrode materials, and the negative electrode materials play a pivotal role in promoting the development of lithium batteries.[2] At the same time, the development of anode materials with good electrical conductivity, high structural stability and high performance is of certain research significance.

A series of anode materials, such as $TiNb_xO_{2.5x+2}$, have multiple redox pairs: Ti^{4+}/Ti^{3+}, Nb^{5+}/Nb^{4+}, Nb^{4+}/Nb^{3+}, which can provide higher theoretical specific capacity, and at the same time, the high operating voltage (1.65 V vs. Li^+/Li) effectively prevents lithium dendrimers and the formation of the SEI film, which reduces the generation of safety problems. The above advantages make this kind of material has been widely explored by researchers at this stage, especially $TiNb_2O_7$, $Ti_2Nb_{10}O_{29}$ and $TiNb_{24}O_{62}$ which are in the research hotspot at this stage. all three materials belong to monoclinic crystal system ReO_3 structure, Ti^{4+} and Nb^{5+} are distributed in the octahedral sites, but with different structural units. And the ability to store Li^+ increases with the increase of Nb content.The formula for the theoretical specific capacity of $TiNb_xO_{2.5x+2}$ and the reaction formula for reversible Li^+ embedding/de-embedding of $TiNb_2O_7$, $Ti_2Nb_{10}O_{29}$ and $TiNb_{24}O_{62}$ can be expressed as follows:

ISSN: 2414-1895 DOI: 10.6919/ICJE.202404_10(4).0025

$$TiNb_2O_7+xLi^++xe^-\leftrightarrow LixTiNb_2O_7\ (0\leq x\leq 5)$$
$$Ti_2Nb_{10}O_{29}+xLi^++xe^-\leftrightarrow Li_xTi_2Nb_{10}O_{29}\ (0\leq x\leq 22)$$
$$TiNb_{24}O_{62}+xLi^++xe^-\leftrightarrow Li_xTiNb_{24}O_{62}\ (0\leq x\leq 49)$$

2. Modification Options

Although $TiNb_xO_{2.5x+2}$ series materials have been demonstrated as anode materials that can be used to transport lithium ions, the fact that both Ti and Nb elements are in the highest valence state leads to poor electronic conductivity and poor ion diffusivity of such materials, which results in poor electrochemical performance and inhibits the application of the materials at high current densities.[3] In order to solve the existence of such problems, rational structural design and adjustment of effective electron/ion transfer paths, such as realizing material nanosizing, material compositing and doping modification, are effective initiatives to enhance the cycle life and multiplicity performance of batteries.[4]

2.1 Constructing Nanomaterials

Constructing the nanosized material can increase the specific surface area of the material, which makes the contact area between the active material and the Li in the electrolyte increase, and the active sites increase, which is conducive to the rapid transport of Li^+. In addition to this, the construction of nanosized materials with stable structures can enhance the compaction density of the materials and resist the damage to the electrode materials caused by the embedding and dislodging process of Li^+ at high current densities.

Tao[5] synthesized $TiNb_2O_7$ consisting of an intercrystalline mesoporous skeleton by sol-gel method using an ionic liquid as a nanoporous structure oriented template. The mesoporous structure can be stabilized by mitigating the repetitive mechanical stresses and volume changes during the embedding and dislodging of lithium ions, and the stabilization of the crystal structure of the material contributes to the long cycling and resisting the structural damages caused by the high current densities, so that this type of material can maintain a specific capacity of 210 $mAh\cdot g^{-1}$ under a current density of 50 C current density can still maintain a discharge specific capacity of 210 $mAh\cdot g^{-1}$.

Liu[6] prepared $Ti_2Nb_{10}O_{29}$ microspheres using solvent heating and heat treatment, which still reached a capacity of 185 $mAh\cdot g^{-1}$ after 200 cycles at a current density of 10 C. Liu and his members[7] synthesized mesoporous $TiNb_2O_7$ (M-TNO) using surface solvent heating and calcination, which exhibited a higher specific capacity and a longer cycle life due to the shortening of the charge and ion transport distance , M-TNO exhibits a smaller charge transport resistance, while the voids of the material can alleviate the volume change during cycling, thus presenting a higher discharge specific capacity and a longer cycle life. The first discharge specific capacity at 0.1 C corresponds to 319 $mAh\cdot g^{-1}$ and the discharge specific capacity at 10 C corresponds to 155 $mAh\cdot g^{-1}$.

2.2 Material Coating Modification

Because the conductivity of $TiNb_xO_{2.5x+2}$ series is not good, the method of carbon coating can be used to form a carbon layer on the surface of $TiNb_xO_{2.5x+2}$ series materials, so as to make the materials internally interconnected to form a conductive network. Accelerating electron transport is conducive to improving the conductivity of $TiNb_xO_{2.5x+2}$.

Wang et al.[8] prepared electrospinning technology $TiNb_2O_7$@C Fibers are synthesized by carbonizing glucose at high temperatures to achieve carbon coating $TiNb_2O_7$@C It exhibits a high discharge specific capacity of 245 $mAh\cdot g^{-1}$ at 0.5 $A\cdot g^{-1}$. This material is composed of linear morphology composed of nanoparticles connected at different sites, which can fully utilize the longitudinal one-dimensional electron transfer, achieve good contact between electrons and ions, and effectively improve the rate performance of the electrode. Meanwhile, carbon coating helps to stabilize Nb^{4+}, thereby improving cycling stability.

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Dopamine self-polymerization of $TiNb_2O_7$@C coated with dopamine was obtained by Gong et al.[9] Specific data are shown in Figure 1.The modified material prepared showed excellent multiplicity performance when the controlled addition of dopamine was appropriate. When the controlled current density was 0.1 C, the corresponding discharge specific capacity was 294 $mAh \cdot g^{-1}$, and the corresponding capacity retention of the material was 91% after 400 cycles at a high current of 10 C. The material was also found to have a high capacity retention rate. This is hypothesized to be due to the introduction of the carbon layer, which enhances the conductivity of the initial blank material, resulting in an overall enhancement of the electrochemical performance.

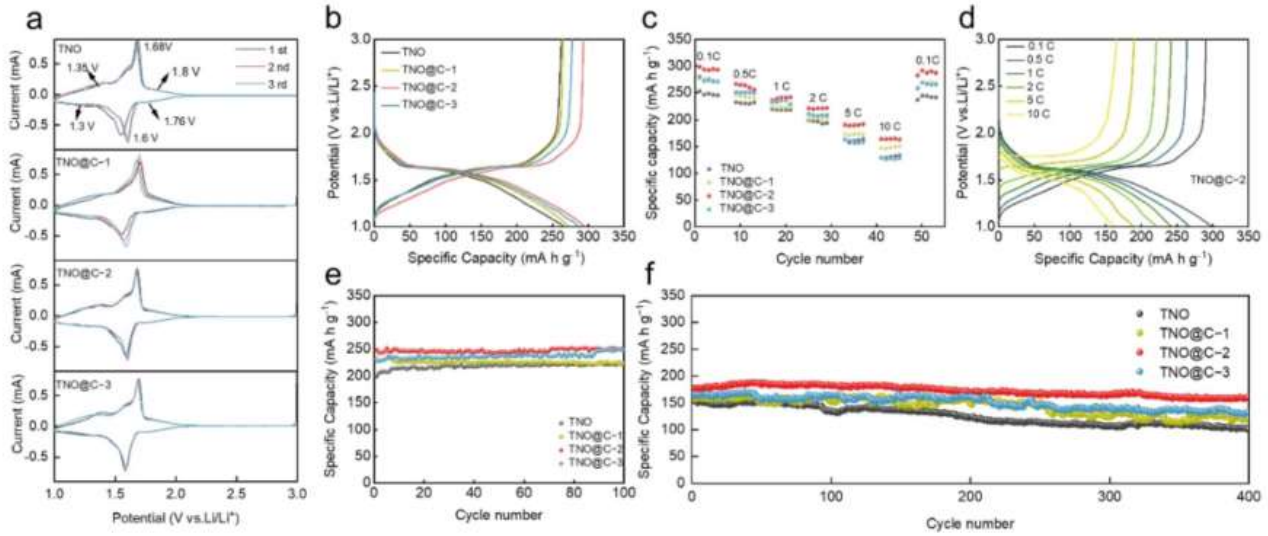

Figure 1. (a) CV curves of $TiNb_2O_7$ and $TiNb_2O_7$@C at 0.1 $mV \cdot s^{-1}$; (b) discharge/charge curves of $TiNb_2O_7$ and $TiNb_2O_7$@C at 0.1 C; (c) rate performance of $TiNb_2O_7$ and $TiNb_2O_7$@C; (d) discharge/charge curves of $TiNb_2O_7$@C-2 at different multiplicities; (e) cycle stability of $TiNb_2O_7$ and $TiNb_2O_7$@C-2 at (f) 10 C[9].

Li et al.[10] introduced a facile electrostatic spinning technique to prepare carbon-coated $Ti_2Nb_{10}O_{29}$ hollow submicron materials with one-dimensional morphology structure. At a current density of 1 C, the material prepared by the electrostatic spinning technique can provide a discharge specific capacity of 259.7 $mAh \cdot g^{-1}$, and the capacity decay rate of the material is only 0.013% during long-term charge/discharge cycling. Therefore, the use of this electrostatic spinning technique can improve the reaction efficiency and make the obtained material have a controllable morphology, which can ensure the stable capacity and long life of the anode material during the cycling process.

2.3 Material Doping Modification

In order to improve the crystal and electronic structure within a material, doping is a common strategy to accelerate charge transfer. By means of doping it is possible to make the doped elements enter the crystal structure and widen the lattice spacing.[11]

Paik and his colleagues[12] prepared porous $TiNb_2O_7$ microspheres by solvothermal method and nitrided the material using ammonia, the nitriding effect reduces the bandgap energy and promotes the electron transport, and the interaction between the two improves the transport kinetics of ions and electrons. When the controlled current density was 100 C, a discharge specific capacity of 143 $mAh \cdot g^{-1}$ was presented, and the capacity retention rate was 91% after 1000 cycles.

Bian et al.[13] synthesized Sn_x-$TiNb_2O_7$ materials with Sn-doped $TiNb_2O_7$ by solid-phase method to investigate the effect of Sn^{4+} on the electrochemical properties of $TiNb_2O_7$ materials. It was confirmed by XRD diffractograms that Sn doping can increase the lattice spacing and the diffusion coefficient of lithium ions in the $TiNb_2O_7$ materials, and the Sn doping exhibits better kinetic reaction processes

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and higher reversibility of redox reactions compared with the unmodified $TiNb_2O_7$ materials. Among them, the $Sn_{0.01}$-$TiNb_2O_7$ material exhibits the smallest polarization, the lowest charge transfer impedance and higher ion diffusion coefficient.

Lei et al.[14] synthesized H_2MoO_4-derived Mo-doped $TiNb_2O_7$ materials by combining the solvothermal method with the calcination method, which can still maintain 80% of the specific capacity of discharge after 500 cycles at a current density of 2.6 C. After 500 cycles at a high current density of 10 C, the material can still maintain the microsphere structure, which suggests that the Mo doping has certain advantages for applications.

3. Conclusion

Niobate anode materials, with such advantages as, have strong application value, and are expected to be used in related fields for energy storage with high safety and high discharge specific capacity. However, niobate has seriously limited the development of this type of material due to its low conductivity, so researchers have been advancing the niobate by means of morphology modulation, outer layer coating and inner core doping. In the future development process, how to adopt lower cost to enhance the conductivity of the material is the main direction.

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