The synthesis of lithium pentatitanate powders for lithium-ion batteries

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Abstract. The lithium-ion rechargeable batteries (LIBs) have been widely used in portable electronic devices such as mobile phones, smartphones, laptops, and computers. It is also very promising to use these batteries as power sources for electric vechicles. However, current LIBs using graphite (carbon) as the anodic material exhibit poor rate performance induced by their low Li diffusion coefficient, poor cycle life and serious safety issues caused by the solid electrolyte interphase (SEI) film. Developing high-performance electrodes materials has been an essential component of the current endeavor for the next generation of LIBs. In the search for safe materials with good rate capability and excellent cyclic stability, spinel $Li_4Ti_5O_{12}$ (LTO) has been extensively studied as an ideal anodic material for LIBs owing to several inherent advantages. LTO has been investigated as a powerful anode material, because of its high thermal stability and high structural stability (zero-strain insertion material) in the charge-discharge process.

$Li_4Ti_5O_{12}$ samples can be synthesized by various methods. For large-scale application, a conventional solid-state reaction is used to synthesize $Li_4Ti_5O_{12}$, because of its scale-up ability, low cost, and non-requirement of sophisticated apparatus. As a rule, LTO is obtained by solid-state reaction (SSR) between rutile or anatase (TiO_2) and lithium carbonate Li_2CO_3 or lithium hydroxide LiOH at temperatures above 800°C, while a long isothermal exposure is required to ensure a high content of the $Li_4Ti_5O_{12}$ phase in the product. The use of nano-structured precursors, as well as the pretreatment of precursors in high-energy ball-milling or planetary mills, allows to intensify the process of solid-state reaction.

An alternative to SSR it is a very simple and promising glycine-nitrate method that allows the synthesis of nanostructured homogeneous powders.

The disadvantage of LIBs is the relatively low electronic conductivity (especially at high cycling rates). Therefore, it is necessary to improve the technology of manufacturing the anode material to enhance the characteristics of LTO, in particular, to increase the specific capacity and stability during cycling by increasing the electronic conductivity and diffusion rate. This can be achieved through the use of nanostructured powders, control of their morphology, doping, creation of coatings and composites.

The main goal of the present work was to determine the optimal conditions for the synthesis of LTO by the solid-phase method from a mechanoactivated mixture of lithium carbonate and rutile, and by the modified glycine-nitrate method, providing the production of an anode material with a specific capacity close to the theoretical one.

The main tasks were:

1. To establish the effect of the duration of mechanical activation of a mixture of lithium carbonate and rutile in a Pulverisette-5 planetary mill and heat treatment conditions on the characteristics of powders and anode material;

2. To study the kinetic patterns of the second stage of lithium pentatitanate synthesis;

3. To study the effect of the ratio of reagents, the amount of additives of metal ions (zirconium, aluminum, lanthanum, manganese) and heat treatment on the characteristics of powders and anode material based on lithium pentatitanate synthesized by the modified glycine-nitrate method.

Scientific novelty:

1. The effect of mechanical activation of a mixture of rutile and lithium carbonate in a Pulverisette-5 planetary mill on their characteristics has been studied. It is shown that mechanical activation is accompanied by partial decomposition of lithium carbonate with the release of CO_2, disordering of the crystal lattice of components and accumulation of defects.

2. For the first time, kinetic patterns were studied for the second stage of solid-phase synthesis of lithium pentatitanate, a mathematical model was selected (the Johnson-Mehl-Avrami equation) and the activation energy of the process (393 ± 20 kJ/mol) was determined.

3. The influence of the duration of mechanical activation of a mixture of lithium carbonate and rutile on the characteristics of the anode material has been established. It is shown that an increase in the duration from 1 to 60 minutes contributes to an increase in the content of the target phase in the material and an increase in the specific capacity by 5 times (up to 170 mAh/g at 0.5C). A further increase in the duration of mechanical activation leads to secondary aggregation of powders and a decrease in electrochemical characteristics.

4. For the first time, the influence of conditions for the synthesis of lithium pentatitanate powders by the modified glycine-nitrate method on their characteristics has been studied. It is established that the powders synthesized under optimal conditions are monophasic and have a high specific capacity. It is shown that the capacity of a material is largely determined by its phase composition.

The theoretical and practical significance of the work. Optimal modes of synthesis of monophase lithium pentatitanate by the solid-state method have been established: the duration of mechanical activation of precursors is 60 minutes, the temperature is 800°C (2 h). The anode material synthesized under these conditions demonstrates stable operation when cycling with various current loads (170 mAh/g at 0.5C and 98 mAh/g at 10C), and can be used in a lithium-ion battery for high-current applications.

The modified glycine-nitrate method under optimal conditions (G/N = 0.7, $CitH_3/\sum Me$ = 0.37-0.56, t = 700°C, t = 2 h) synthesized $Li_4Ti_{4,975}Mn_{0,025}O_{12}$, with a high specific capacity (200 mAh/g at 0.5C), which can be used as an anode material of a lithium-ion battery for low-current applications.

Defence Provisions:

1. The influence of the duration of mechanical activation of a mixture of lithium carbonate and rutile and heat treatment conditions on the characteristics of powders;
2. Kinetic patterns of the second stage of solid-state reaction of lithium pentatitanate from mechanically activated mixtures;
3. The influence of conditions for the synthesis of lithium pentatitanate-based powders by the modified glycine-nitrate method on their characteristics;
4. The electrochemical properties of synthesized anode materials based on lithium pentatitanate.