

Synchrotron X-ray diffraction in situ study of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesis from rutile and anatase

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Abstract. The comparative study of solid state synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ from rutile and anatase as initial reagents was carried out using the method of in situ synchrotron radiation dynamic diffractometry. Initial samples were obtained by mechanical treatment of Li_2CO_3 and TiO_2 (anatase or rutile modifications). It was found that on the first stage an intermediate $\beta\text{-Li}_2\text{TiO}_3$ phase forms in the reaction system. On further heating the process of formation of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase from $\beta\text{-Li}_2\text{TiO}_3$ and TiO_2 is limited by lithium cation diffusion through the $\beta\text{-Li}_2\text{TiO}_3$ phase. Reaction strongly accelerates at temperatures above 800 °C. Using nano-sized anatase precursor, well-crystallized LTO with smaller grain size may be obtained at lower temperatures.

1 Introduction

The lithium-titanium oxide $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) with the spinel structure is considered as one of the promising anode material for lithium-ion batteries (LIB) due to its relatively low redox potential of 1.55 V (versus Li/Li^+) and the effect of zero deformation upon insertion/extraction of lithium cations[1-4]. However, low electronic conductivity (10^{-13} S/cm) and a moderate value of diffusion coefficients of lithium ions (10^{-13} - 10^{-9} cm^2/s) in LTO limit its rate capacity, especially in the bulk phase [5-7]. The main methods for obtaining electrode materials of this type are solid state synthesis, hydrothermal and sol-gel methods [9-11]. Each of these methods has certain advantages and disadvantages. Solid state technique is characterized by simplicity, possibility to obtain pure single phase LTO material and relatively low cost. However, this method requires long-term sintering and leads to the uncontrolled aggregation of particles and the formation of large grains. As a result, the performance of the anode material based on LTO is impaired. In most cases, a decrease in the temperature and time of calcination results in weak crystallinity and high concentration of lattice defects [11-12]. Therefore, there is a problem to obtain the sample with small particle size and high crystallinity using solid state technique. One approach to solve this problem is the using initial reactant characterized by lower grain size and higher reactivity. In the case of LTO synthesis such reactants could be various polymorph

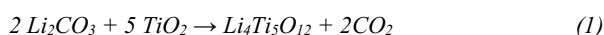
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modifications of titanium dioxide, e.g. rutile and anatase. In the present work, the comparative study of solid state synthesis of LTO from rutile and anatase as initial reagents was carried out using the method of in situ synchrotron radiation (SR) dynamic diffraction.

2 Experimental

Commercial powders of Li_2CO_3 (LLC Soyuzkhimprom, 99.9% pure) and two types of TiO_2 were used to study the effect of the type of the polymorph and the particle size on the process of the formation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. A sample obtained from titanium dioxide with the rutile structure (commercial material, LLC Soyuzkhimprom, 99 % pure) hereinafter referred as LTR. The anatase modification of TiO_2 was obtained hydrothermally in our laboratory as reported earlier [13] and comprised nanocrystalline material with the average grains size of 15 ± 5 nm. The sample prepared from anatase modification of TiO_2 is referred as LTA. Both the samples, LTR and LTA, were obtained according to the reaction:



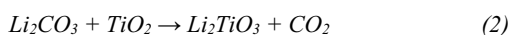
Mixtures of Li_2CO_3 and TiO_2 (rutile or anatase) taken in a stoichiometric ratio were preliminarily ground in a high-energy ball mill AGO-2 for 5 minutes and specific power of 40 g [14].

In situ X-ray time-resolved studies were carried out at the station 5bof VEPP-3 storage ring [15]. One-coordinate detector OD-3 recorded diffraction patterns [16]. A wavelength of monochromatic radiation was 1.51 Å at the scanning angle range 2θ of 33–57 deg. The mechanically treated samples were placed in a special furnace which was heated with a constant rate 10 C/min. The exposure time of OD-3 was set to 1 minute.

High-temperature synthesis was carried out under identical conditions for each sample under study.

3 Results and Discussion

Fig. 1 shows the diffraction patterns for the LTA sample, where the nanostructured TiO_2 anatase was used as a precursor. To facilitate analysis, only diffraction patterns obtained at 50 K intervals are shown in the Figure. The diffraction patterns of the initial mixture obtained at a low temperature correspond to a nanosized anatase, as evidenced by the low intensity of reflections and their width. This range of angles includes some reflections of Li_2CO_3 with low intensity. However, due to the small particle size of particles and low intensities, these reflections are not clearly detected. On heating, starting from 470 °C, the intensity of the TiO_2 anatase phase decrease and a new phase appear, indexed as monoclinic $\beta\text{-Li}_2\text{TiO}_3$. Evidently, the following reaction starts at this temperature:



The intensity of $\beta\text{-Li}_2\text{TiO}_3$ increases with temperature up to 800 °C. At a temperature of 730 °C reflections of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase appears on the diffraction patterns. The most clearly it is seen for the reflection of (400) crystallographic plane of the spinel lattice which appears as a shoulder of the peak attributed to the $\beta\text{-Li}_2\text{TiO}_3$ phase. With further heating, the peaks become narrower, which indicates to the growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. At a temperature of 800 °C, anatase transforms into rutile, which is thermodynamically stable form of TiO_2 . At temperatures above 800 °C the intensities of peaks attributed to the rutile,

β - Li_2TiO_3 phases begins to decrease, and at 900 °C these peaks are not observed. As a result, well-crystallized sample of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel phase is formed at 900 °C.

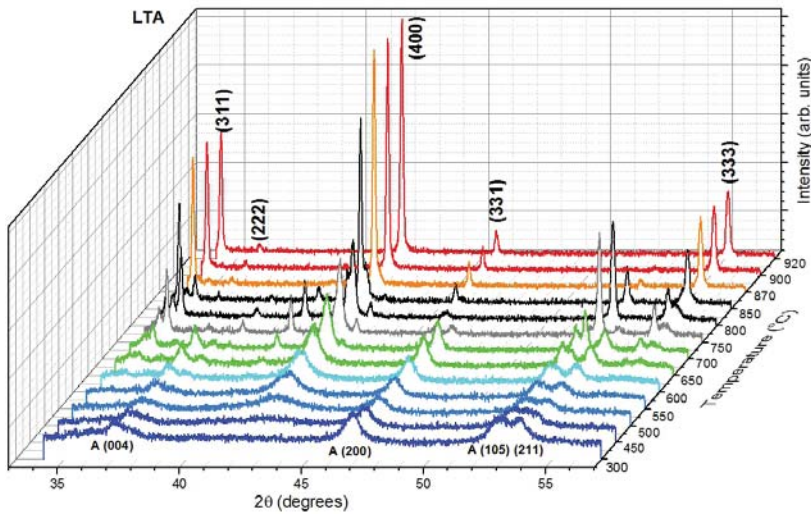
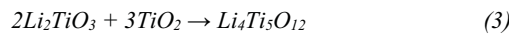


Fig. 1. Diffraction patterns of the sample LTA obtained using nanocrystalline anatase as a source of titanium. The reflections attributed to anatase phase are designated by symbols A. The reflections of the spinel phase of LTO are also indicated.

The observed changes in the intensities of the reflections of the phases TiO_2 , Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ may be explained by the reaction



which proceeds at temperatures above 730 °C and completes at 900 °C.

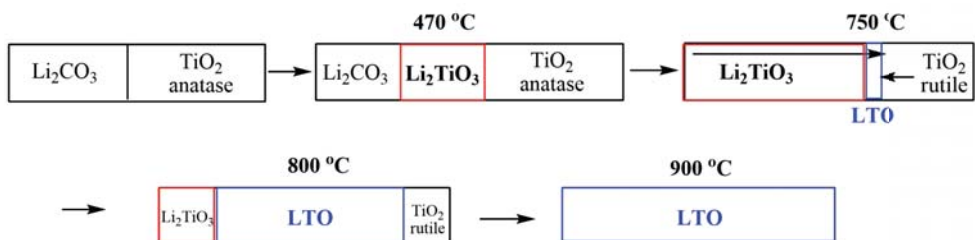


Fig. 2. Scheme of the process of formation of LTO phase from lithium carbonate and anatase.

Fig. 2 shows a simplified scheme for the formation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. On the first stage at $T > 470$ °C, a layer of lithium-rich Li_2TiO_3 phase forms on the $\text{Li}_2\text{CO}_3/\text{TiO}_2$ (anatase) interface as a result of the reaction (2). This reaction is almost complete at 800 °C, whereas the reaction (3) leading to formation of LTO is limited by slow diffusion of lithium cations to the surface of anatase through the insulating layer of Li_2TiO_3 . In turn, the anatase phase transforms to the rutile phase at 800 °C. At the second stage at $T > 740$ °C, due to faster

diffusion of lithium ions through the Li_2TiO_3 layer, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase start to form at the $\text{Li}_2\text{TiO}_3/\text{TiO}_2$ (anatase or rutile) interfaces. At the final stage, lithium diffusion is not limited and rutile phase reacts with Li_2TiO_3 according to reaction (3) with formation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Fig. 3 shows the diffraction patterns for the LTR sample obtained using rutile polymorph of TiO_2 as an initial reagent. After mechanical treatment in a ball mill the reagents remained well-crystallized as the reflections of both the phases Li_2CO_3 and rutile are clearly seen. On heating at 600 °C the peaks attributed to the monoclinic phase $\beta\text{-Li}_2\text{TiO}_3$ appear on the diffraction patterns. The intensity of the reflections of $\beta\text{-Li}_2\text{TiO}_3$ phase increases up to temperature of 900 °C.

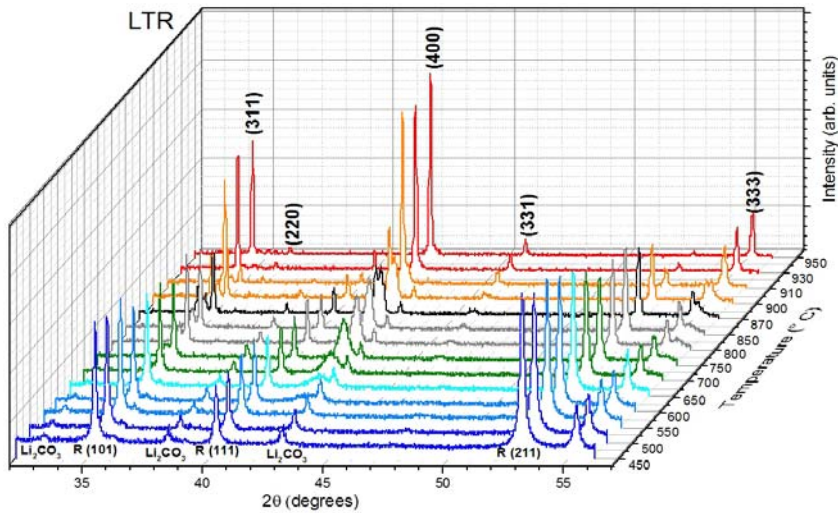


Fig. 3. Diffraction patterns of the sample LTR obtained using rutile as a source of titanium. The reflections attributed to the rutile phase are designated by symbols R. The reflections of Li_2CO_3 and spinel phase of LTO are also indicated.

At a temperature of 870 °C a reflection of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase appears as a shoulder of the most intense peak related to the Li_2TiO_3 phase. The intensity of the reflections of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase increases very rapidly with increasing temperature. In parallel, the intensities of peaks attributed to phases of rutile and Li_2TiO_3 strongly decrease. At a temperature of 950 °C intense reflections of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase can be observed, but a weak diffraction peaks related to the rutile phase are still present. Since in the diffraction experiments the heating was carried out with a rather high rate of 10 deg/min, the reaction (3) was not complete due to kinetic reasons. Usually, to obtain a single phase sample of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ from rutile, sintering of the initial sample at 950 °C for 5 hours is required. As seen from Table 1, the grain size of the LTO phase in the samples under study increases with the heating temperature. It should be noted that LTO prepared from anatase precursor has smaller grain size compared to the sample obtained from rutile. As the temperature increases, this difference becomes less expressed.

Table 1. The change in the average grain size of the LTO in the samples formed from anatase and rutile precursors (LTA and LTR, respectively) during the heating. The grain size values were determined from the X-ray diffraction peaks width using the Rietveld method.

Temperature (°C)	850	900	950
Sample:	The grain size (nm):		
LTA	220 ± 9*	301 ± 10	637 ± 6
LTR	383 ± 11*	482 ± 9*	650 ± 12*

* the sample is not monophasic

4 Conclusions

The comparative study of solid state synthesis of LTO from rutile and anatase as initial reagents was carried out using the method of in situ synchrotron radiation (SR) dynamic diffractometry. A sequence of phase transformation observed in the experiments allowed one to propose a scheme of the chemical processes, which take place during the synthesis. It was found that on the first stage an intermediate β -Li₂TiO₃ phase forms in the reaction system. On further heating, the process of formation of the Li₄Ti₅O₁₂ phase from β -Li₂TiO₃ and TiO₂ is limited by lithium cation diffusion through the β -Li₂TiO₃ phase. Reaction strongly accelerates at temperatures above 800 °C. It was shown that the TiO₂ precursor influences the grain size of Li₄Ti₅O₁₂ particles. Using nano-sized anatase precursor, well-crystallized LTO with smaller grain size may be obtained at lower temperatures. At the temperature of the synthesis above 950 °C the grain size of LTO reaches values of nearly 640 nm, regardless of the precursor used.

The work was supported by the State assignment of ICCM SB RAS, project FWUS-2021-0007. Authors used facilities of CCU STSTI based on USI “VEPP-4 - VEPP 2000” at Budker Institute of Nuclear Physics SB RAS, Novosibirsk, Russia.

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