



Influence of the conditions of a solid-state synthesis anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ on its electrochemical properties of lithium cells

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Abstract. Lithium–titanium spinel is a promising electrode material for high power and environmentally friendly batteries. We did research on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) samples, which were synthesized via solid-state reaction at various conditions in a temperature range from 800 to 900°C and they were investigated by XRD, SEM, IS, cyclic voltammetry and the galvanostatic charge–discharge tests. X-ray diffractions show that all of the samples have a spinel structure with Fd-3m space group with a small amount of impurities TiO_2 (anatase). Lithium ion batteries with LTO-based electrode exhibit excellent reversible capacity of $\sim 180 \text{ mAh g}^{-1}$ in the current density range from 0.1 to 1 C. As an electrode material for rechargeable lithium-ion batteries, LTO-F demonstrates the best rate and cyclic performance from all of the studied samples.

Keywords. Spinel; lithium batteries; anode; $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

1. Introduction

Since the 70s of the twentieth century, the synthesis and characterization of spinels' material $\text{Li}_{3+y}\text{Ti}_{6-y}\text{O}_{12}$ ($0 \leq y \leq 1$) were the aim of the research due to its superconductivity at relatively high transition temperature [1]. A comparison of a commercial lithium ion battery cycle life in an electrical vehicle was made with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ present by Han *et al* [2]. The process of intercalation and de-intercalation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was discovered about a decade later. Anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has a spinel structure with space group Fd-3m, the cell contains eight units $(\text{Li})^8(\text{Li}_{1/3}\text{Ti}_{5/3})^{16d}\text{O}_4^{32e}$ where tetrahedrons 8a are entirely occupied by lithium, octahedra 16d are split between lithium and titanium in an atomic ratio 1:6 and the space 32e is filled with oxygen. One unit of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is capable of electrochemical and reversible uptake of three lithium ions, going to $\text{Li}_7\text{Ti}_5\text{O}_{12}$, which has the structure of a rock salt. For the synthesis of LTO solid phase method is used mainly because of its simplicity, low cost and adequately leavened crystals at a relatively high sintering temperature (800–1000°C). TiO_2 is widely used as a titanium source while lithium carbonate (Li_2CO_3) or LiOH is used as a lithium source for the synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Titanium oxide (IV) (TiO_2) is mixed with an appropriate amount of lithium source and then the mixture is sintered at a high temperature (800–1000°C) from 8 to 12 h [3,4]. Studies showed that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obtained by various methods of synthesis can be of nanometric [5,6] or larger [7] size. Lithium cells with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode of theoretical capacity, about 175 mAh g^{-1} , typically reach a capacity of about 100 mAh g^{-1} and a relatively low potential. It is believed that the electrochemical capacity of

LTO can be significantly improved by cautiously controlling the particle size of the active material and by reducing the diffusion length of the electrons inside the lithium particles. This can be achieved easily by sol–gel method [8,9]. In this method, both dissolved titanium and lithium salt are added to a solvent (for example, ethanol) to form a gel. The solvent is then evaporated to give nanoscale precursor particles, which are then annealed at a temperature of 800–1000°C, to eventually obtain a final $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It was proved that the materials of nanometric size can achieve a theoretical performance and high potential. However, the energy density of batteries using nano-dimensional anode materials $\text{Li}_4\text{Ti}_5\text{O}_{12}$ remains problematic for two reasons. First, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ working at a potential of 1.55 V ($\text{Li}^+|\text{Li}$), which is approximately 1.5 V higher than the potential of graphite anodes. Second, high porosity and low density of charging electrodes by using materials of nanometric size may lead to a further reduction of the volumetric energy density of the battery. A practical approach to increase the charge density is the synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials comprising micrometric secondary particles, which consist of primary particles of nanometric size. Micrometric particles used for the synthesis of the material improve the volume density and the charge density of the electrodes, while the particles of nanometric size still have all the advantages associated with powder of nanometric $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In this approach, TiCl_4 or the other soluble titanium salt is used as the starting material to form a porous TiO_2 precursor. The porous structure precursor sintered at high temperature is degraded. Removal of water from crystallizing during the synthesis of the powder contributes in keeping the tunnel structure in the molecule. The tunnel structure captures the non-aqueous

electrolyte and increases the availability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ towards lithium ions.

A further modification of the method of anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesis is the addition of a carbon source such as tar to the original material, e.g., a mixture of mesoporous TiO_2 , LiOH and tar [10–13]. During the sintering process, the addition of the carbon source at reducing conditions at high temperatures produces a carbon coating layer on the surface of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Anode material for lithium ion-based $\text{Li}_4\text{Ti}_5\text{O}_{12}$ compound is a very interesting material for high-voltage cells, easy synthesis and above all safety. The aim of this study is to determine the influence of synthesis methods of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material on its electrochemical properties. To achieve the desired objective active material of various parameters of synthesis was manufactured. Then it was tested in terms of purity of samples, the attainable gravimetric capacity and transport properties.

2. Experimental

2.1 Synthesis of LTO

The process of producing the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ began with weighing the starting materials, namely: Li_2CO_3 and (IV) (TiO_2) in suitable proportions. Names and parameters of the materials' synthesis process are presented in table 1.

Thereafter, the material was milled in a mortar with a small amount of propanol to the desired consistency. Thereafter, the whole was re-weighed and divided into two parts. Then, the powder was broadcasted with the ceramic balls in the mixing container. The milling process of the one part of the material was performed once for 20 min and the second portion of the material was milled for 20 min five times at intervals of 10 min in order to cool the material. After completion of the grinding process, the material had to be cooled to room temperature and later by manual pressing with the usage of the relevant dye the powder was shaped in the form of a small disk. Then the disc-shaped material was sintered in a resistance furnace at a temperature of 900 and 800°C.

2.2 Preparation of electrode

Preparation of electrode with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was performed in a glove box (Mbraun) under an argon atmosphere and the impurity level of less than 0.1 ppm O_2 and H_2O . Previously synthesized pills were inserted into the argon chamber. The

electrode consisted of 70% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (active material), 15% graphite, 10% carbon black and 5% of PVDF (polyvinylidene fluoride). In order to obtain consistency of the black paste a few drops of N-methylcopirolidone were added. The electrode materials were mixed with a magnetic stirrer for about 12 h. After removing from the chamber the mixture was in the form of a thin film, which was broadcasted on aluminium foil and then put into a vacuum dryer. The material was dried for 1 h at a temperature of 70°C and then removed in order to cool down to room temperature. After some time discs of a diameter of 1.35 mm were cut down with the usage of the punch and hammer. Then, each cut disc was compressed in an uniaxial press at a pressure of 700 kg cm^{-2} and then annealed at a temperature of 80°C in the argon chamber.

2.3 The construction of a lithium-ion cell with $\text{Li}_4\text{Ti}_5\text{O}_{12}$

In literature research results for $\text{Li}|\text{Li}^+|\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells are described. Since lithium potential is equal to -3.04 V and for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ it is 1.55 V, in such cell lithium performs a role of anode and consequently the spinel is the cathode. As an electrolyte 1M LiPF_6 (in EC:DEC = 1:1) was used. Cell cases CR2032 were used in order to close the cell.

2.4 Measurement methods

Structure measurement of collected material in the form of a powder was analysed by X-ray diffraction (XRD). XRD measurements were performed in 10–110° range with Cu K α radiation using PANalytical Empyrean diffractometer.

Samples' pellets conductivity was measured using impedance spectroscopy with frequency response analysers, Solatron 1260 and Solatron 1296, from room temperature to 250°C in order to determine the electrical properties of the material.

The process of cyclic charging and discharging the battery: cells were tested using the KEST 32 K amperostat by 32 channels. Prepared cells were tested several times with the use of the charging/discharging process. Currents of different values were used.

3. Results and discussion

3.1 Structure

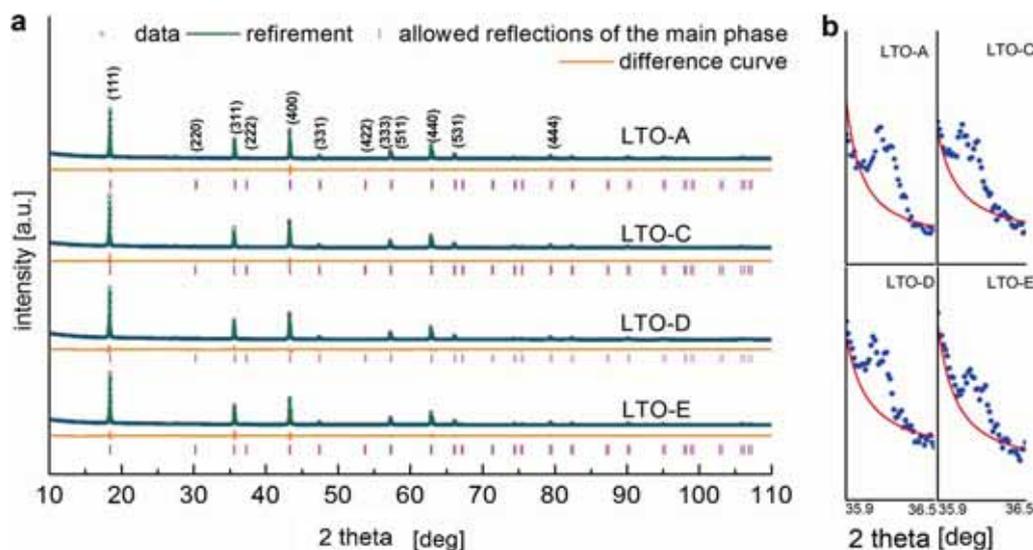
Produced $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was examined by XRD in order to verify the present phases. The space group of materials is

Table 1. Preparation conditions for studied samples.

Sample names	LTO-A	LTO-B	LTO-C	LTO-D	LTO-E	LTO-F
Milling times (20 min)	1	5	1	1	1	5
Temperature of synthesis (°C)	900	900	900	900	900	800
Heating period (h)	4	4	8	12	24	24

Table 2. Phase content of obtained samples including the preparation conditions.

Samples	Preparation conditions : (milling period/heating temperature/heating period)	Structure parameters		Phase content (%)	
		Cell volume (\AA^3)	Lattice parameter a (\AA)	$\text{Li}_4\text{Ti}_5\text{O}_{12}$	TiO_2
LTO-A	20 min/4 h/900°C	584.58	8.3615	97.93	2.07
LTO-B	100 min/4 h/900°C	584.36	8.3604	98.71	1.29
LTO-C	20 min/8 h/900°C	584.37	8.3604	98.47	1.53
LTO-D	20 min/12 h/900°C	584.38	8.3605	98.60	1.40
LTO-E	20 min/24 h/900°C	584.46	8.3607	98.62	1.38
LTO-F	100 min/24 h/800°C	584.57	8.3614	98.94	1.06

**Figure 1.** The diffraction patterns of LTO-A, LTO-C, LTO-D and LTO-E samples: (a) range of 10–110 (2θ) and (b) approximation in the range of 35.9–36.5 (2θ).

Fd-3m. The study demonstrates that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples are contaminated by other phases to a very small extent. The results are shown in the charts and table 2.

Network parameters were determined by adjustment with the numerical Rietveld method using the GSAS/EXPGUI [14,15] software. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ identification was made on the basis of the reference code: 04-0007-9267, while TiO_2 on the basis of reference code: 04-007-4874. Contamination with another phase is often found in the literature. At work [6], the authors showed that in the synthesized material (calcination 700°C/16 h) the ratio Li:Ti was not 0.8, as assumed, but 0.784, the rutile phase is present. Xie *et al* [8] detected anatase presence in material calcined at temperature 600° and 650°C for 20 h. At work [16] the authors found LTO and additionally $\text{Li}_{2.39}\text{Ti}_{3.4}\text{O}_8$. In all cases sol–gel preparation method was used. Mohammadi and Fray [17] studied LiO– TiO_2 system in detail specifying conditions at which $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2TiO_3 i TiO_2 phases co-exist.

Figure 1 presents the diffraction patterns of LTO-A, LTO-C, LTO-D and LTO-E samples: (a) range of 10–110 (2θ) and (b) approximation in the range of 35.9–36.5 (2θ), which are

visible to the maxima of TiO_2 . The samples do not include Li_2TiO_3 . The maximum amount of impurities present in the material with the shortest time of synthesis, LTO-A, where there are other phases—the resulting reflections of TiO_2 in the amount of 2.07%. Other samples have a small amount of these impurities (about $1.3 \pm 0.3\%$). The shortest synthesis time at 900°C leads to the increase of TiO_2 amount present in the sample. Extension of the time of grinding from 20 to 100 min and extension of the heating time of 4–24 h did not result in the change of total TiO_2 being reacted. The best results in terms of purity of the sample gave a prolonged soaking for 24 h while decreasing the temperature to 800°C.

Construction of the lithium titanium spinel is essential to the process input and output of lithium ions into the structure of oxide material. As many as three moles of lithium ions can participate in the process of intercalation/de-intercalation. Phase transition from spinel to the structure of rock salt causes only a slight shrinkage of the lattice parameter, of 8.3595–8.3538 \AA , with only a 0.2% change in cell volume. A cell parameter of prepared powders falls within the range 8.3604–8.3615 \AA . The elementary cell volume is in the

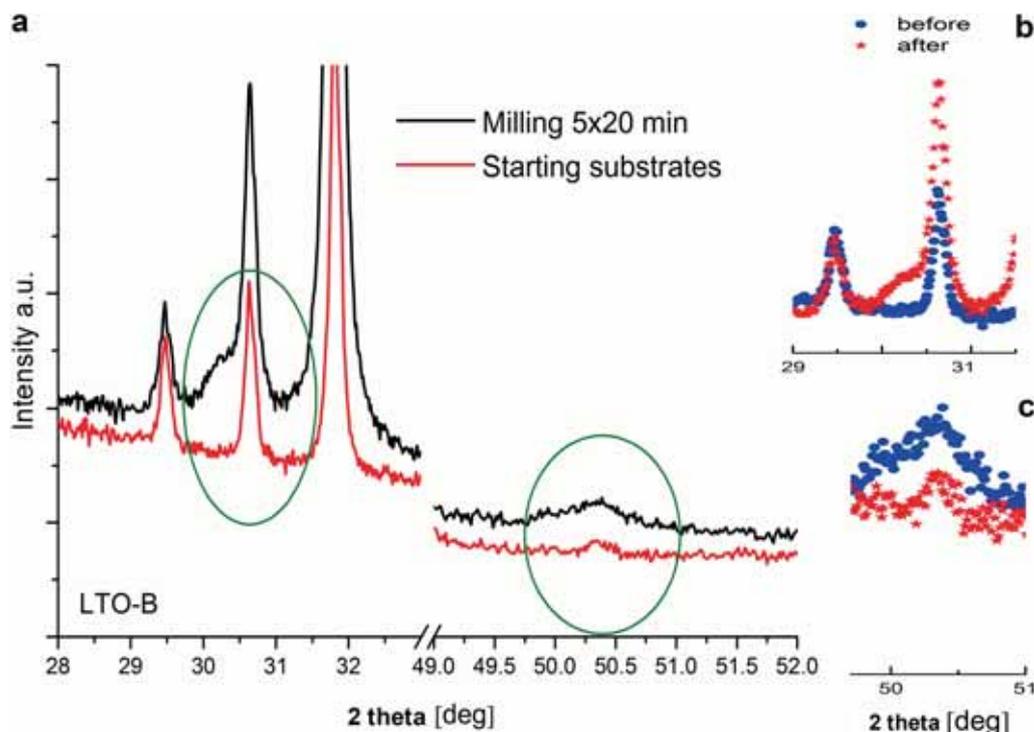


Figure 2. (a) The diffraction pattern of the LTO-B sample, the angular range 28–33 (2θ) and 49–52 (2θ) range, and additionally in the narrowed range of 29–31.5 (2θ) range (b), and 49.7–51 (2θ) range (c).

range of 584.36–584.58 Å³. This confirms that the structural parameters are consistent with the literature. It can be considered that the materials obtained are characterized by a consistent structure.

In turn figure 2 shows the diffraction pattern of the sample LTO-B, the angular range 28–33 (2θ) and 49–52 (2θ) and additionally in the narrowed range of 29–31.5 (2θ) (b) and 49.7–51 (2θ) range (c). The two largest peaks are derived from ZrO₂ doped Y—the material from which they are made into balls and added to the grinding chamber. As can be seen, extending the grinding time up to 100 min causes the appearance of this contamination. Therefore, this is an additional reason to refrain from a long time grinding in the mill substrates. A similar effect was noticeable for sample LTO-F.

Figure 3 shows SEM images of the LTO-A, LTO-B, LTO-E and LTO-F microstructure samples with the same scales $\times 10,000$ (a) and 50,000 (b), respectively. It seems that on the basis of images in approximately 10,000, the most porous material is LTO-F. Magnification of 50,000 times confirms this conclusion. LTO-E results in the worst images—virtually no visible agglomerates are a very heterogeneous structure. In the LTO-A sample you can see the outlines of agglomerates and a porous structure, but the LTO-B sample seems to be better. Only the LTO-F contains agglomerates of about 200 nm diameter and larger. SEM images confirm that the soaking temperature of 900°C is not optimal because it leads to a significant distortion of the grains and thus faces difficulties in the transport of lithium intercalation in the battery.

The use of a temperature of 800°C leads to the formation of porous structures with separate agglomerates. A similar to LTO-F morphology of commercial powder Li₄Ti₅O₁₂ was observed by Wang *et al* [18].

3.2 Conductivity

In figure 4 the impedance spectra of LTO-C, LTO-D, LTO-E and LTO-F samples (in the form of pellets) are present. Semicircles in high frequencies are responsible for charge transport for which the diagram corresponds to the replacement resistor R1. In the impedance spectrum it is shown that the charge transport decreases with increasing temperature, which suggests that the material Li₄Ti₅O₁₂ may have high electrochemical activity at high temperatures. The fitted last line in the field of low frequency is attributed to the diffusion of lithium ions to the thickness of the electrode material, which is called the Warburg diffusion. Observing the structure of the sample, one can expect LTO-F to have the best transport properties of the material. LTO-F sample characterizes with the lowest material resistance, whereas the LTO-E sample characterizes with the highest one. An order of conductivity magnitude is 10⁻⁷ S cm⁻¹ and ionic conductivity was observed. Most of the research is for the battery and not for the electrode material (for example [19]). In addition, resistivity is greatest for LTO-E (100 Ω cm). The resistivity of the LTO-C and LTO-D is about half the size and the LTO-F

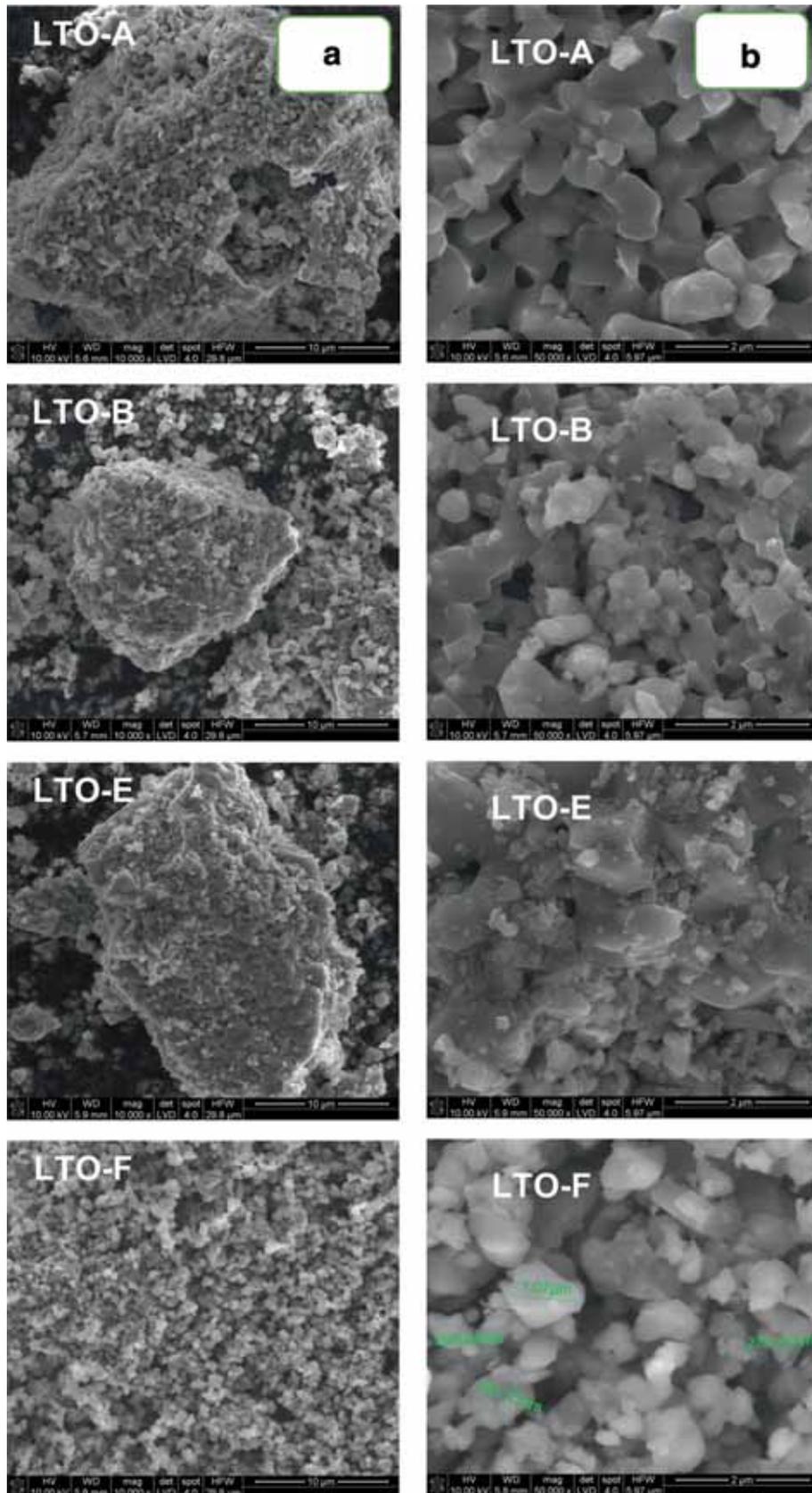


Figure 3. SEM images of microstructure of the LTO-A, LTO-B, LTO-E and LTO-F samples with the same scales $\times 10\,000$ (a) and $\times 50\,000$ (b).

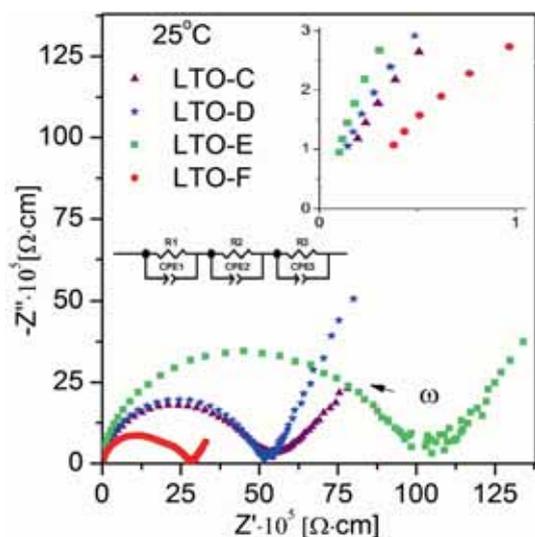


Figure 4. Impedance spectroscopy of the LTO samples in the form of pellets.

powder has the lowest resistivity ($30 \Omega \text{ cm}$). The conductivity of all samples is in the range from 10^{-6} to 10^{-7} S cm .

3.3 Electrochemical properties

Cells were tested using galvanostatic cyclic charging/discharging (lithium intercalation and de-intercalation to the anode). Figure 5 presents discharge/charge cycles for LTO-B, LTO-C, LTO-D, LTO-E and LTO-F samples. LTO-A ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ milled for 20 min and synthesized at a temperature of $900^\circ\text{C}/4 \text{ h}$) was tested with currents of C/10, C/5 and C/2 and showed very high capacity close to the theoretical one (175 mAh g^{-1}). Unfortunately, for the current of 1 C capacity decreased by 60% (obtained value: 60 mAh g^{-1}) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ milled once for 20 min, synthesized for 8 h at a temperature of 900°C (LTO-C) achieved very good results up to the capacity of 20 C. Capacity at about 140 mAh g^{-1} , which represents 80% of the theoretical capacity was maintained with the current 1 C. Capacity at about 130 mAh g^{-1} was maintained with the current 2 C. Currents of 5 C and 10 C charged batteries to 60% of the theoretical capacity of about 100 mAh g^{-1} and the capacity decreased drastically with higher currents of 20 C (about 60 mAh g^{-1}) (figure 6).

The cell with an anode material that was grinded once for 20 min and synthesized for 12 h at 900°C (LTO-D) reached a maximum capacity of about 120 mAh g^{-1} (70% of the theoretical value) at a current of C/10. Further examination only reduced the capacity of the battery, while the current of 5 C resulted in the capacity reaching only about 30 mAh g^{-1} , which is about 17% of the theoretical capacity. The LTO-E sample's maximum capacity (about 120 mAh g^{-1}) is achieved at the lowest charging current of C/10. Capacity at about 50% of the theoretical value was maintained with the current 2 C.

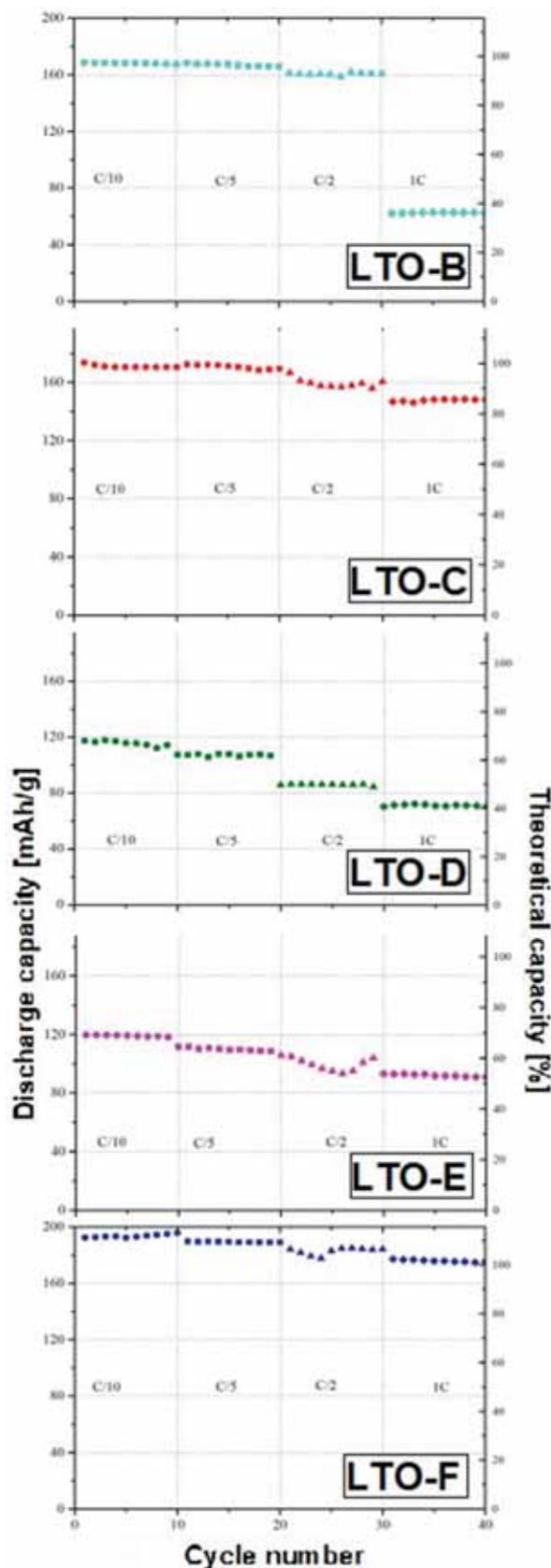


Figure 5. Discharge/charge cycles for LTO-B, LTO-C, LTO-D, LTO-E and LTO-F samples.

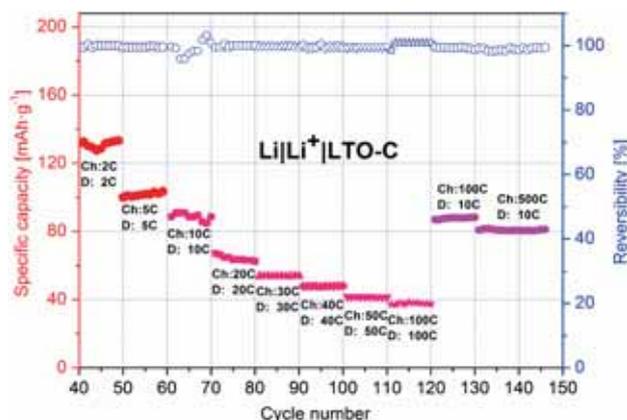


Figure 6. The cycling performance of LTO-C at the same and different discharge (D) and charge (Ch) rates.

A battery with electrode material, which has been milled five times for 20 min and synthesized for 24 h at 800°C (LTO-F) showed excellent electrochemical properties. The gravimetric capacity in current range from C/10 to 1 C oscillates around the theoretical capacity and even slightly above it at the lowest possible load currents of the battery. With the currents 2 and 5 C one can already see a noticeable drop in the capacity, however, for such a high current discharge, the capacity is maintained at a satisfactory level, that is, 80 and 55% of the theoretical capacity, respectively.

To sum up, the results of the cyclic charging and discharging test of the battery showed that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a very promising material in terms of gravimetric capacity. The sample with the highest capacity obtained was a sample, which was milled five times and synthesized for 24 h at 800°C.

In contrast, the battery with the sample once milled and sintered at a temperature of 900°C for 8 h proved to be the most stable battery at high current charging and discharging. In comparison to the five samples, which were milled and sintered at a temperature of 900°C for 4 h and the sample, which was grounded once at 900°C for 8 h; it can be seen that the grinding time does not significantly affect the gravimetric capacity.

Putting together the batteries differing at the time of synthesis, 8, 12 and 24 h respectively, it can be seen that the longer the time of synthesis by the greater battery the capacity decreases. The difference between the battery sample grounded once at 900°C for 8 h and the sample that was milled once at 900°C for 12 h is of the order of 30%. Batteries with the milled material once at 900°C for 24 h and milled five times at a temperature of 900°C for 24 h also differ in the gravimetric maximum capacity. Decrease of the temperature of 100°C resulted in a rapid increase in capacity.

The battery containing the LTO-C was tested at higher current rates. It was subjected to cycles of charging (C)/discharging (C): 10/10, 20/20, 30/30, 40/40, 50/50 and 100/100 and additionally 100/10 and 500/10 (figure 6). It

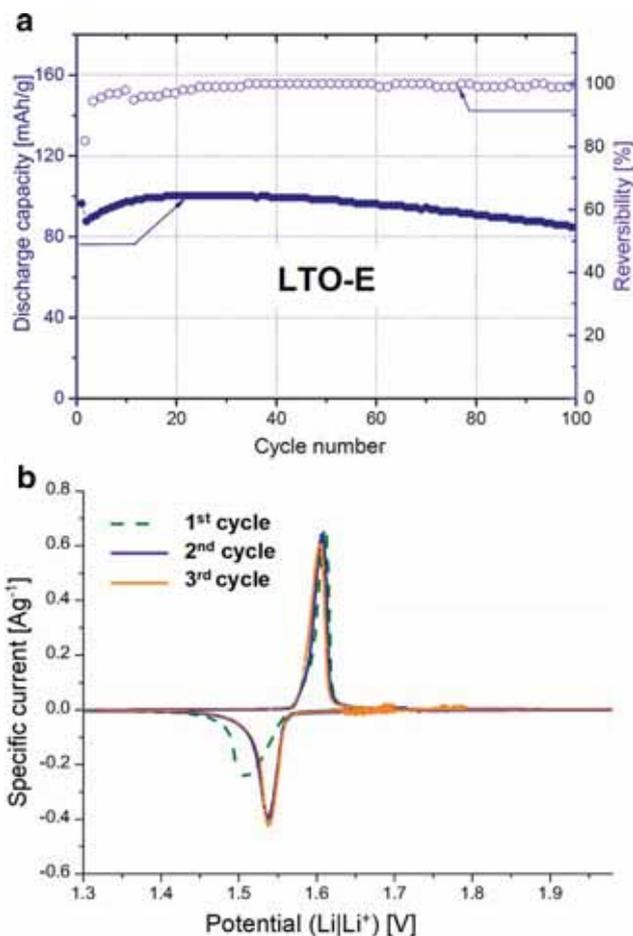


Figure 7. (a) Cycling performance of the LTO-E sample (discharge capacity and reversibility as a function of successive cycles, discharge/charge current rate, 10 C); (b) cyclovoltammograms of 1st, 2nd and 3rd cycle's of $\text{Li}|\text{Li}^+|\text{LTO-C}$, at scan rates 0.02 mVs^{-1} for LTO-C sample.

was found that for cycles of 10/10, 100/10 and 500/10, the discharge capacity is about 50% of the theoretical capacity and the reversibility is practically 100%.

Cycling performance of the LTO-E sample: discharge capacity and reversibility as a function of subsequent cycles and discharge/charge current rate 10 C is shown in figure 7a. Among the samples tested, LTO-E has the worst electrochemical and transport properties but even in this case it can be seen that the material is stable in terms of discharge capacity and reversibility.

Cyclovoltammograms shown in figure 7b were made for the first, second and third cycle of charging and discharging the battery with $\text{Li}|\text{Li}^+|\text{LTO-C}$. The profile of the first cycle is different than the next two charging terms, which are practically identical. In the case of the discharge process all profiles are the same. Therefore, this material is stable. The anodic and cathodic processes are not the same, as shown by asymmetrical charging and discharging curves with respect to each other. The polarity is relatively small, about 0.1 V.

4. Conclusions

To achieve results and to acquire adequate knowledge to write the thesis, study has been conducted in the chemical and physical/high level specialized laboratories. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystallites were synthesized using different parameters of the synthesis. Prepared material purity determination was studied with the usage of the XRD method (X-ray diffractometer).

The following conclusions were made

- the anode material LTO-E is a single-phase material;
- another very pure material is LTO-F sample, which was milled five times after 20 min and synthesized for 24 h at 800°C. This XRD pattern shows that the samples are almost single phase, it contains 99% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase and about 1% TiO_2 phase;
- compared LTO-C and LTO-D that was once grinded and synthesized at temperatures of 900°C for 12 and 24 h, respectively, which showed a 1.53 and 1.4% TiO_2 phase;
- the most contaminated sample was LTO-A sample, which contained in a second phase 2.07% TiO_2 . Sample pellets were characterized using impedance spectroscopy (IS) method, which demonstrates the transport properties of synthesized samples. Impedance spectroscopy studies show:
 - that the LTO-E, LTO-F and LTO-B samples presented the best ion- and electron-conductivity;
 - from the comparative charts for the specific samples one can see deterioration of transport properties within temperature increase.

The galvanostatic tests showed the capacity of the samples LTO-B, LTO-C, LTO-F and reached the theoretical capacity of the cycling currents of C/10 to 1 C. LTO-C and LTO-D samples achieved much poorer results, yielding a capacity of about 120 mAh g^{-1} at a discharge current C/10.

To conclude, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material is a very promising electrode material for lithium-ion batteries. It is confirmed with the results presented in this work. The material has characterized with a very good gravimetric capacity, good ion- and

electron-conductivity and above all, it is unrivalled in terms of security.

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