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Transport and Electrochemical Properties of Li$_4$Ti$_5$O$_{12}$-Li$_2$TiO$_3$ and Li$_4$Ti$_5$O$_{12}$-TiO$_2$ Composites

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Abstract: The study demonstrates that the introduction of the electrochemically inactive dielectric additive Li$_2$TiO$_3$ to LTO results in a strong decrease in the grain boundary resistance of LTO-Li$_2$TiO$_3$ (LTC) composites at a low concentration of Li$_2$TiO$_3$. With the increase in the concentration of Li$_2$TiO$_3$ in LTC composites, the grain boundary resistance goes through a minimum and increases again due to the growth of the insulation layer of small Li$_2$TiO$_3$ particles around LTO grains. For LTO-TiO$_2$ (LTT) composites, a similar effect was observed, albeit not as strong. It was found that LTC composites at low concentration of Li$_2$TiO$_3$ have unusually high charge–discharge capacity exceeding the theoretical value for pure LTO. This effect is likely to be caused by the occurrence of the electrochemical activity of Li$_2$TiO$_3$ in the vicinity of the interfaces between LTO and Li$_2$TiO$_3$. The increase in the capacity may be qualitatively described in terms of the model of two-phase composite in which there is the interface layer with a high capacity. Contrasting with LTC composites, in LTT composites, no capacity enhancement was observed, which was likely due to a noticeable difference in crystal structures of LTO and TiO$_2$ preventing the formation of coherent interfaces.

Keywords: Li$_4$Ti$_5$O$_{12}$-Li$_2$TiO$_3$; Li$_4$Ti$_5$O$_{12}$-TiO$_2$ composites; solid-state synthesis; ionic conductivity; grain boundary resistance; excess charge capacity

1. Introduction

Lithium titanate batteries (LTBs), which use lithium titanate Li$_4$Ti$_5$O$_{12}$ (LTO) as the anode material, open up new possibilities for the energy storage of lithium-ion batteries (LIBs) with a number of economical as well as ecological aspects. These batteries are characterized by relatively fast recharge, low internal resistance, high charge and discharge rates, long cycle life, high reliability and safety. At present, Toshiba, YABO and Altair Nanotechnologies produce LTBs for electric vehicles and energy storage. Research on LTO-based materials began about 30 years ago to replace graphite as the negative electrode in LIBs [1,2]. LTO is already known to be crystallized in cubic syngony (space group Fd-3m) and have AB$_2$O$_4$ spinel structure presented as Li[Li$_{1/6}$Ti$_{5/6}$]$_2$O$_4$. The volume change of the unit cell associated with insertion/extraction of lithium in/out Li$_4$Ti$_5$O$_{12}$ (0 < x < 3) is very small (~0.2%). Therefore, Li$_4$Ti$_5$O$_{12}$ is regarded as a zero-strain material for lithium insertion that offers high stability during cycling (up to 10,000 cycles) without significant loss of capacity [3–5]. High potential plateau around 1.55 V (vs. Li$^+/Li$) exceeds the reduction potential of most electrolyte solvents, and thus avoids the formation of lithium dendrites on the anode surface. This ensures the safety of LIB with an LTO anode, in contrast to LIB with a graphite anode [4–7]. However, the main limitation for the wide practical use of LTO is poor electronic and ionic conductivity, which, according to various reports, ranges from 10$^{-13}$ to 10$^{-7}$ S cm$^{-1}$ [8–10].

Heterogeneous doping is one of the most promising approaches to materials modification. This approach makes it possible to obtain composite solid electrolytes with high ionic...
conductivity [11–14]. The introduction of heterogeneous additives can lead not only to improved charge-discharge characteristics, but also to an increase in the specific capacity of the electrode material. As Krajewski et al. (2016) reported, CV and EIS measurements show an increase in Li$^+$ chemical diffusion coefficient values with increasing the amount of Ag nanoparticles in the LTO powder up to 3% wt. [15]. Galvanostatic charge/discharge studies (Krajewski et al., 2017) demonstrate the enhanced electrochemical properties of Li$_4$Ti$_5$O$_{12}$ powder after its modification with Ag–Cu nanoparticles mixture, namely ca. 12.5% increase in specific capacity retention and ca. 19 mAh g$^{-1}$ increases in specific capacity at a current rate of 10 C were observed [16]. The authors suggest the reason of improved electrochemical properties to be surface activation through contact with conductive nanoparticles, which leads to an increase in the electrochemically active electrode surface as well as in the reaction rate. Dielectric phases can also be used as heterogeneous additives for doping electrode materials. It was recently discovered that LTO-based composite electrode materials with additives of the electrochemically inert phase Li$_2$TiO$_3$ have better electrochemical characteristics compared to pure LTO-based anode material [17,18].

The phase $\beta$-Li$_2$TiO$_3$ with monoclinic structure (space group C2/c) is the most studied modification of Li$_2$TiO$_3$ [19,20]. The values of the specific discharge capacity of $\beta$-Li$_2$TiO$_3$ depend on the particle size or the discharge rate. For micrometer-sized Li$_2$TiO$_3$ particles, the discharge capacity is about 12–15 mAh g$^{-1}$ for the first five discharge cycles [21,22]. The specific discharge capacity of nanofibers on the first cycle is 18.77 mAh g$^{-1}$ [21]. Large capacity loss on the first cycle and less strong but continuous decrease in capacity on the next 10 cycles indicates that Li$_2$TiO$_3$ is electrochemically inactive, and its reversible capacity can be neglected. Nevertheless, the addition of Li$_2$TiO$_3$ as a structurally compatible dopant to LTO [17,18] demonstrates not only a better rate capability but also higher specific discharge capacities (216 mAh g$^{-1}$ at 0.1 C and 194 mAh g$^{-1}$ at 0.5 C) as compared to LTO (175 mAh g$^{-1}$) [23]. As Li$_2$TiO$_3$ is an electrochemically inert material, the authors (Li et al., 2017; Bhatti et al., 2016) suggest that Li$_2$TiO$_3$ inclusions could improve the lithium ion conductivity of the composite nanofibers and, in addition, enable intercalating of more lithium ions to the interfaces of the composite nanofibers which can be considered as additional lithium storage sites [23,24].

In this study, LTO-Li$_2$TiO$_3$ and LTO-TiO$_2$ composites have been chosen as systems for studying the electrophysical and electrochemical properties. Both composites were obtained by solid-phase synthesis by changing the Li/Ti ratio. In the case of Li excess, the Li$_2$TiO$_3$ phase is formed as an additional phase, and in the case of Ti excess the composites contain TiO$_2$ phase.

2. Materials and Methods

2.1. Synthesis

The samples of LTO, LTO-Li$_2$TiO$_3$ and LTO-TiO$_2$ composites were synthesized by solid-state reaction. As the initial reagents, Li$_2$CO$_3$ (Chemical grade, Rare Metals Plant Inc., Novosibirsk, Russia) and TiO$_2$ (rutile, Chemical grade, Interkhim Inc., Novosibirsk, Russia) powders were used. For the synthesis of LTO, LTO-TiO$_2$ and LTO-Li$_2$TiO$_3$ composites the initial reagents were taken in amount corresponding to different atomic ratio to Li:Ti. The final products of synthesis obtained at the Li:Ti ratios equal to 2.8:5, 3.2:5, 3.6:5, 4.5, 4.2:5, 4.4:5, 4.6:5, 4.8:5 and 5.2:5 were denoted as LTT-3, LTT-2, LTT-1, LTO, LTC-05, LTC-1, LTC-15, LTC-2 and LTC-3, respectively. The initial reagents were preliminarily mixed in agate mortar and then mechanically treated in a high-energy planetary mill AGO-2 in steel jars by steel balls (diameter 8 mm) for 5 min at a rate of 400 rpm. Prior milling of a small portion of the mixture was milled in order to line surfaces of the jar and the balls with the treated material in order to avoid possible contamination of the treatment products by the wearing material from the jar and balls. After treatment, the mixtures were pressed into pellets and annealed at 950 °C for 5 h.
2.2. Characterization

Phase identification of the prepared samples was carried out by X-ray diffraction (XRD) using a D8 Advance powder diffractometer (Bruker) in Θ-Θ-geometry under Bragg–Brentano focusing with CuKα radiation source and a one-dimensional Lynx-Eye detector with a nickel filter. The ICDD-PDF2 database was used for phase identification. Quantitative phase analysis and refinement of the structure parameters were performed by the Rietveld method using the Topas 4.2 program.

The morphology of the LTC samples was studied by high-resolution transmission electron microscopy (HREM) on a dual-corrected transmission electron microscope Themis Z (Thermo Fisher Scientific) with an accelerating voltage of 200 kV and a limiting resolution of 0.07 nm and 0.06 nm.

To study the transport properties and ionic conductivity, the test samples were compressed into the pellets at 20 MPa and sintered at 950 °C for 5 h in air. Silver paste electrodes were deposited on the surfaces of the pellets. Electrical measurements were carried out in air in the temperature range from 35 to 250 °C in forevacuum in a stepwise isothermal mode using a HP-4284A Precision LCR Meter in the frequency range of 30 Hz–1 MHz.

To identify electrochemical properties, 80 wt.% of active material under study, 6 wt.% of carbon black, 4 wt.% of nanotubes, and 10 wt.% of PVDF binder were mixed and dispersed in N-methylpyrrolidone (NMP) to form slurry. Copper foil 15 µm in thickness was coated with the resulting slurry and dried in a vacuum oven at 120 °C overnight. The total loading of the film coating was approximately 1.5–2 mg cm⁻². The coated foils were punched into 8 mm diameter disks to obtain the working electrode, and dried at 120 °C overnight under vacuum before being placed in the glovebox for cell assembling. The electrolyte used was a mixture (1:1 by mass) of 1 M LiPF₆ solution in ethylene carbonate (EC) and dimethylcarbonate (DMC). The electrodes were assembled inside a dry glovebox chamber into coin cell of the CR2032 type with the metallic lithium counter electrode. Charge/discharge curves were recorded on ACK 2.5.10.1 analyzer in the galvanostatic mode at various current densities between 1.0 and 2.5 V (vs. Li⁺/Li⁰).

3. Results

3.1. Structural Studies

Figure 1 shows the XRD patterns of LTO, LTC-2 and LTT-2 composites, corresponding to the two-phase systems Li₄Ti₅O₁₂-Li₂TiO₃ and Li₄Ti₅O₁₂-TiO₂, respectively. The content of the impurity phases β-Li₂TiO₃ or TiO₂ depends on the relative amount of lithium in the initial mixture. The excess Li content (atomic ratio of Li/Ti > 4/5) produces a two-phase system Li₄Ti₅O₁₂-Li₂TiO₃ as shown in Figure 1b whose patterns include overlapping XRD peaks of monoclinic β-Li₂TiO₃ (ICDD-33-0831) Figure 1 a and cubic Li₄Ti₅O₁₂ (ICDD-49-0207) Figure 1 c. If lithium is deficient (atomic ratio of Li/Ti < 4/5), two-phase systems Li₄Ti₅O₁₂-TiO₂ as shown in Figure 1 d are formed when the impurity phase is rutile TiO₂ with orthorhombic structure (ICDD-21-1276) (Figure 1e).

The Li₂TiO₃ and TiO₂ phases concentrations in the composites determined from the XRD profiles were 4.6; 9.7; 16.4; 19.7 and 28.4 wt.% for LTC-05, LTC-1, LTC-15, LTC-2 and LTC-3 composites and 11.6 and 20.3 wt.% for LTT-1 and LTT-2 composites, respectively. These values correlate well with the calculated data presented in Table 1.

Thus, composites with a certain percentage of the additional phase can be obtained by changing the deviation from the stoichiometric ratio Li:Ti = 4:5. Figure 2 shows a detailed part of the XRD patterns in the 2θ range from 41 to 44°. It is clearly seen that by increasing or decreasing the Li content in the initial reagents, it is possible to obtain the final product with a given content of impurity phase of a certain type, which is confirmed by calculations performed by the Rietveld method.
Figure 1. XRD patterns of samples synthesized at different ratios of Li:Ti in the initial mixtures: composite (b) LTC-2 (Li:Ti = 4.8:5), (c) single phase LTO (Li:Ti = 4.0:5) and (d) LTT-2 composite (Li:Ti = 3.2:5) in comparison with the patterns of pure phases (a) Li$_2$TiO$_3$ and (e) TiO$_2$ (rutile).

Table 1. The calculated values of relative concentrations of components in composites.

| Sample | Atomic Ratio Li:Ti | Mass Fraction of TiO$_2$ or Li$_2$TiO$_3$ | Volume Fraction of TiO$_2$ or Li$_2$TiO$_3$ |
|--------|--------------------|------------------------------------------|------------------------------------------|
| LTT-3  | 2.8:5              | 0.272                                    | 0.235                                    |
| LTT-2  | 3.2:5              | 0.179                                    | 0.152                                    |
| LTT-1  | 3.6:5              | 0.088                                    | 0.074                                    |
| LTO    | 4.5                | 0                                        | 0                                        |
| LTC-05 | 4.2:5              | 0.040                                    | 0.032                                    |
| LTC-1  | 4.4:5              | 0.079                                    | 0.064                                    |
| LTC-15 | 4.6:5              | 0.117                                    | 0.097                                    |
| LTC-2  | 4.8:5              | 0.155                                    | 0.129                                    |
| LTC-3  | 5.2:5              | 0.230                                    | 0.194                                    |

Figure 2. The sections of XRD patterns showing both the reflections of LTO and the impurity phase in the pure LTO sample and (a) in LTC-1, LTC-2, LTC-3 and (b) LTT-1, LTT-2, LTT-3 composites.
3.2. Ionic Conductivity

The electrical properties of the synthesized materials were studied through the method of impedance spectroscopy. For the analysis of the impedance spectra at the temperature range from 35 to 250 °C the equivalent circuit was proposed as shown in Figure 3.

![Figure 3. The equivalent circuit used to interpret the results of electrical measurements.](image)

The circuit includes three impedances connected in series related to the impedance of the bulk material, $Z_b$, the grain boundary impedance $Z_{gb}$, and the electrode impedance $Z_e$. Each element of the circuit corresponds to a different stage of ion transport or polarization in the material. Bulk impedance and grain boundary impedances include two elements: resistance ($R_b$ and $R_{gb}$) and constant phase element ($CPE_b$ and $CPE_{gb}$). The electrode impedance is described by the constant angle element $CPE_e$, a special case of which is the Warburg impedance. The volume resistance of the sample is related to the value of the volume conductivity, $\sigma_b$, by the ratio $\sigma_b = 1/R_b (d/S)$, where $d$ is the pellet thickness and $S$ is the electrode area. The value of the bulk conductivity is described by the Arrhenius equation:

$$\sigma_b = A_b \cdot \exp \left( -\frac{E_b}{kT} \right)$$

(1)

The grain boundary resistance $R_{gb}$ can be represented as $\sigma_{gb} = 1/R_{gb} (d/S)$, where $\sigma_{gb}$ is a parameter which has the dimension of conductivity and also obeys the Arrhenius dependence:

$$\sigma_{gb} = A_{gb} \cdot \exp \left( -\frac{E_{gb}}{kT} \right)$$

(2)

The $CPE_b$, $CPE_{gb}$, and $CPE_e$ values are defined by the equations

$$CPE_b = Y_b \cdot (i\omega)^{\alpha_b}$$

(3)

$$CPE_{gb} = Y_{gb} \cdot (i\omega)^{\alpha_{gb}}$$

(4)

$$CPE_e = Y_e \cdot (i\omega)^{\alpha_e}$$

(5)

where $Y_b$, $Y_{gb}$ and $Y_e$ are constants; $\alpha_b$, $\alpha_{gb}$ and $\alpha_e$ are the exponents ($0 < \alpha_b$, $\alpha_{gb}$, $\alpha_e < 1$) and $\omega$ is the angular A.C. frequency. Empirically, it was found that the best agreement
between theoretical and experimental data is observed assuming that CRE\textsubscript{\textit{b}} values depend on temperature according to the expression:

\[ Y_{gb} = \frac{Y_{gb}}{T} \cdot \exp \left( -\frac{(1 - \alpha_{gb}) E_{gb}}{kT} \right) \]  

(6)

The reasons for this dependence remain unclear and require additional theoretical analysis which is beyond the scope of this study. The expression for the Warburg impedance was used as the electrode impedance, i.e., it was assumed that in all cases \( \alpha_e = 0.5 \).

Thus, 11 independent parameters were used to fit the theoretical dependencies (1–6) to the experimental data in the temperature range 35–250 °C: \( A_b, E_b, \epsilon_b, Y_b, \alpha_b, A_{gb}, E_{gb}, \epsilon_{gb}, Y_{gb}, \alpha_{gb}, Y_e \). The data obtained at 30 different A.C. frequencies in the frequency range of 30 Hz–1 MHz at 20–30 temperatures, i.e., a total of 600–900 experimental points, were used for the analysis. Fitting was performed using Mathcad 11.0 and UTCMathcad 15.0 software.

Typical fitting results are demonstrated in Figure 4a,c,e for samples LTO, LTC-1 and LTT-1, respectively. Figure 4b,d,f show some Nyquist plots for these samples. The numerical values of the equivalent circuit parameters obtained by fitting are shown in Table 2. The first element of the equivalent circuit, \( Z_{gb} \), describing the transport of ions through the volume of the material, is characterized by the volume conductivity with the activation energy \( E_b = 0.47–0.53 \text{ eV} \). This value of the activation energy agrees well with the calculated data presented in the papers [25,26]. The value of LTO bulk conductivity at room temperature determined in this work (1.8 \( \times \) 10\textsuperscript{-8} S cm\textsuperscript{-1}) is within the range reported in the literature: from 8 \( \times \) 10\textsuperscript{-10} [27] to 7.6 \( \times \) 10\textsuperscript{-8} S cm\textsuperscript{-1} [28]. The low conductivity values can be explained by the absence of vacancies in positions 8a and interstitial lithium ions in positions 16c of the spinel structure. The second element of the equivalent circuit, describing the process of ion transport across grains surfaces, is characterized by the grain boundary resistance \( R_{gb} \) with the activation energy \( E_{gb} = 0.90–1.1 \text{ eV} \). This process is limited by the contribution of the grain boundary resistance to the total impedance of the sample. At a high temperature, the electrode polarization effect described by CPE\textsubscript{e} is observed, indicating a predominantly ionic character of conductivity.

The conductivity measured at direct current (assuming negligibly small electrode impedance contribution), \( \sigma_{dc} = (\sigma_b^{-1} + \sigma_{gb}^{-1})^{-1} \), at low temperatures is determined by the value \( \sigma_{gb} \). This value, determined by the grain boundary resistance, depends on the particle size of the samples, the density of the pellet, and the presence of impurities adsorbed on the grain’s surfaces. The addition of a small amount of Li\textsubscript{2}TiO\textsubscript{3} to the LTO leads to a decrease in grain boundary resistance and an increase in values \( \sigma_{gb} \). Despite the difference in the symmetry of the crystal structures, LTO and Li\textsubscript{2}TiO\textsubscript{3} compounds have similar chemical and physical characteristics, their densities at room temperature differ by 1.5%. Consequently, the adhesion between LTO and Li\textsubscript{2}TiO\textsubscript{3} can be expected to be strong, and a good interface contact is formed between the components during sintering of their mixture. In this case, at the LTO/Li\textsubscript{2}TiO\textsubscript{3} interface, additional point defects may form due to interface interaction accompanied by the transfer of cations from one phase to another. Similar processes are characteristic of composite solid electrolytes [12,13].

As a result, the concentration of charge carriers near the interface increases, which leads to a decrease in the grain boundary resistance (or to an increase in \( \sigma_{gb} \) values) for LTC-1, LTC-2 samples. When the concentration of Li\textsubscript{2}TiO\textsubscript{3} increases, small particles of the dielectric phase Li\textsubscript{2}TiO\textsubscript{3} accumulate around LTO particles leading to an increase in the resistance of the grain boundaries and a decrease in the values of \( \sigma_{gb} \). A similar effect is observed in LTT composites, but the relative effect of intergrain resistance reduction in these composites is lower compared to LTC composites.
Figure 4. Temperature dependences of the real part of conductivity, measured at different frequencies (indicated in the plots) (a,c,e) and Nyquist plots (b,d,f) obtained at temperatures 188–190 °C for LTO, LTC-1 and LTT-1 samples. Dots are experimental values; lines are theoretical curves obtained as a result of fitting.
Table 2. Numerical values of the equivalent circuit parameters obtained by fitting.

| Impedance | Parameters of the Equivalent Circuit | Sample |
|-----------|--------------------------------------|--------|
| \(Z_b\)   | \(A_b, \text{S} \cdot \text{K} \cdot \text{cm}^{-1}\)  | LTO   |
|           | \(E_{gb}, \text{eV}\)                | LTC-1 |
|           | \(CPE_{gb}, \text{S} \cdot \text{cm}^{-1} \cdot (\text{Hz})^{\alpha_{gb}}\) | LTC-2 |
| \(\alpha_{gb}\) |                                      | LTC-3 |
| \(Z_{gb}\) | \(A_{gb}, \text{S} \cdot \text{K} \cdot \text{cm}^{-1}\)  | LTT-1 |
|           | \(E_{gb}, \text{eV}\)                | LTT-3 |
| \(\alpha_{gb}\) |                                      | LTC |  |
| \(Z_c\)   | \(CPE_c, \text{S} \cdot \text{cm}^{-1} \cdot (\text{Hz})^{\alpha_c}\) | LTT-1 |
| \(\alpha_c\) |                                      | LTT-3 |
| \(\sigma_b\) at 25 °C, S cm\(^{-1}\)   | 3.3. Electrochemical Properties |
| \(\sigma_{gb}\) at 25 °C, S cm\(^{-1}\) | 2.4. Additives on the Electrochemical Properties |

The experimental values of average voltage and specific discharge capacity for the LTO sample obtained in this work at a discharge rate of 0.1 C are 1.6 V and 166 mAh g\(^{-1}\), respectively. Such values are typical for anode materials based on LTO when measured in the voltage range above 1 V (vs. Li\(^+\)/Li\(^-\)).

The theoretical value of the change–discharge capacitance of the two-phase composite can be obtained for the case when the electrochemical reaction proceeds independently for each component. In this case one can use the sum rule and obtain a linear relationship for the specific capacity related to the mass of the composite, \(Q_{th}\), measured in [mAh g\(^{-1}\)]:

\[Q_{th} = (1 - \omega)Q_1^0 + \omega Q_2^0\]  

where \(\omega\) is the mass fraction of the impurity phase, \(Q_1^0\) and \(Q_2^0\) are the values of the theoretical capacity of individual compounds, LTO and heterogeneous impurity, respectively, in the potential range under study.

The choice of the correct values for the theoretical capacity of \(Q_1^0\) and \(Q_2^0\) depends on the values of the voltage range in which the charge–discharge curves are obtained. When operating in a wider voltage range (below 1 V vs. Li\(^+\)/Li\(^-\)), the discharge curves for pure LTO show an additional plateau at 0.5 V, leading to higher theoretical capacitance values. In the present work, we do not extend the potential range beyond the voltages below 1 V (vs. Li\(^+\)/Li\(^-\)), so a value of 175 mAh g\(^{-1}\) was taken as the theoretical value of \(Q_1^0\). The charge-discharge curves for the Li\(_2\)TiO\(_3\) compound also show a broad plateau in the voltage region of 0.2–1.5 V (vs. Li\(^+\)/Li\(^-\)), which is observed in the nanostructured samples and is characterized by the theoretical capacity value of 170–200 mAh g\(^{-1}\) [30]. However, in the region of voltages above 1 V (vs. Li\(^+\)/Li\(^-\)), used in the present study, the experimental values of Li\(_2\)TiO\(_3\) specific capacity obtained at low charge/discharge rates...
do not exceed 15 mAh g\(^{-1}\) \[17,18\]. It suggests that pure \(\text{Li}_2\text{TiO}_3\) should be electrochemically inert material. In respect to \(\text{TiO}_2\), the ordinary crystalline state of \(\text{TiO}_2\) is known to intercalate only a few amounts of Li. The theoretical value of the capacity of \(\text{TiO}_2\) rutile does not exceed 15 mAh g\(^{-1}\) \[31–33\], which is close to the corresponding value for \(\text{Li}_2\text{TiO}_3\). Therefore, in further calculations it was assumed that the theoretical value of the specific capacity of heterogeneous impurity for both \(\text{Li}_2\text{TiO}_3\) and \(\text{TiO}_2\) is approximately equal to \(Q_2^0 = 15\) mAh g\(^{-1}\).

Figure 5. The charge-discharge curves obtained for the studied samples in the region of potentials 1.0–2.5 V (vs. Li\(^+\)/Li\(^-\)) at the 2-nd cycle at different charge/discharge rates. Corresponding \(\frac{dQ}{dU}\) vs. U curves are presented in the upper plot for (a) LTO, (b) LTC-1, (c) LTC-2 and (d) LTT-1 samples.

Figure 6a shows the variation of the capacity with the mass fraction of the additives in the LTC and LTT composites in comparison with the theoretical relationship, Equation (8). As seen, the capacitance of composites should monotonically decrease with increasing concentration of the additive, \(\text{Li}_2\text{TiO}_3\) or \(\text{TiO}_2\). Nevertheless, at low concentrations of \(\text{Li}_2\text{TiO}_3\) the capacity of LTO-\(\text{Li}_2\text{TiO}_3\) (LTC) composites markedly increases, reaching a value of 187 mAh g\(^{-1}\) which exceeds the theoretical value of the capacity of pure LTO (175 mAh g\(^{-1}\)). With further increase in the concentration of \(\text{Li}_2\text{TiO}_3\) additive, the capacity of composites LTO-\(\text{Li}_2\text{TiO}_3\) decreases to the values expected from Equation (8). In contrast to LTO-\(\text{Li}_2\text{TiO}_3\) composites, the discharge capacity of LTO-\(\text{TiO}_2\) composites monotonically decreases with increasing \(\text{TiO}_2\) concentration in good agreement with the theoretical dependence (8).
Figure 6. The variation of the discharge capacity as a function of the mass fraction of the additive (a) and the discharge rate (b) in LTC and LTT composites. Points are experimental values obtained at the rate of 0.1C in the present work (black, magenta and green points for LTO, LTC and LTT composites, respectively) as well as data (orange points) reported earlier for LTC composites in the paper [23]. Red and green lines are guides for eyes to visualise experimental data for LTC and LTT composites. Blue line corresponds to the theoretical dependences obtained from Equation (8) and magenta lines were obtained using Equation (13) for two values of the LTO grain size: L = 500 nm or 60 nm with parameters $\lambda = 6$ nm, $Q_{01}^1 = 175$ mAh g$^{-1}$, $Q_{02}^2 = 15$ mAh g$^{-1}$ and $Q_{03}^3 = 244$ mAh g$^{-1}$.

4. Discussion

Thus, the effect of increasing the specific capacity reported earlier [23,24] is fully confirmed by the results of the present study. This effect is typical only for the LTO-Li$_2$TiO$_3$ system. The additional contribution of LTO/Li$_2$TiO$_3$ interfaces provides additional sites for the introduction of lithium cations during electrochemical cycling. The effect can only be explained by a sharp increase in the partial capacitance of Li$_2$TiO$_3$ in the composite, which is caused by the interface interaction between Li$_2$TiO$_3$ and LTO and leads to the formation of coherent interfaces (due to a structural similarity) and appearance of the electrochemical activity of Li$_2$TiO$_3$ in the composite. The grain size (more correctly, the size of the coherent regions) of LTO and Li$_2$TiO$_3$, determined using the Rietveld full-profile analysis, are 500 and 80 nm, respectively, large particles of LTO are surrounded by smaller Li$_2$TiO$_3$ grains. High-resolution electron microscopy study showed that in LTC composites Li$_2$TiO$_3$ phase is located near the surfaces of large LTO crystallites. Figure 7 shows electron microscopy image of the Li$_2$TiO$_3$/LTO interface. It is seen that crystal lattices of the adjacent phases coherently stacks without visible defects, pores and cracks.

Let us assume that the composite consists of cubic LTO particles with the size of $L$ covered by a layer of the second phase Li$_2$TiO$_3$ with the thickness of $l$ as shown in Figure 8. In the vicinity of the LTO/Li$_2$TiO$_3$ interfaces there is a layer of the electrochemically active Li$_2$TiO$_3$ phase having a higher specific capacity with a characteristic thickness of $\lambda$. In such approximation, the volume fraction of Li$_2$TiO$_3$ monotonically increases with the thickness of the Li$_2$TiO$_3$ phase. When the concentration of Li$_2$TiO$_3$ is small (at $l \leq \lambda$) practically all volume of this phase gets into the interface region. At higher concentrations (at $l > \lambda$) only part of Li$_2$TiO$_3$ phase remains electrochemically active.
Then, the volume fractions of LTO, Li$_2$TiO$_3$ and the interface phase of Li$_2$TiO$_3$, $f_1$, $f_2$ and $f_S$, respectively, can be calculated varying the thickness of the interface region, $\lambda$, from zero to infinity at the fixed value of the interface position, $L$. The theoretical value of $\lambda$ is $500$ nm or $60$ nm, $p_1 = 3.4$ g cm$^{-3}$; $p_2 = 4.0$ g cm$^{-3}$ and assuming that $\lambda = 8$. In the vicinity of the LTO/Li$_2$TiO$_3$ interfaces there is a layer of the electrochemically active Li$_2$TiO$_3$ phase having a higher specific capacity with a characteristic thickness of $l$. Lines correspond to the crystallographic planes (200) of LTO and (400) or (−313) planes of Li$_2$TiO$_3$. The interface position is roughly indicated by a dotted line. At higher concentrations (at $l > \lambda$) only part of Li$_2$TiO$_3$ phase remains electrochemically active.

Figure 7. An HRTEM image obtained from the near-surface area of the LTC composite particle. Lines correspond to the crystallographic planes (200) of LTO and (400) or (−313) planes of Li$_2$TiO$_3$. The interface position is roughly indicated by a dotted line.

Figure 8. A simplified model of the LTO-Li$_2$TiO$_3$ composite.
Then, the volume fractions of LTO, Li$_3$TiO$_3$ and the interface phase of Li$_2$TiO$_3$, $f_1$, $f_2$ and $f_3$ can be estimated using dimensionless parameters $\alpha = \lambda/L$ and $\beta = \lambda/L$, respectively, as follows:

$$f_1 = \left(1 - \frac{2\alpha}{1 + 2\alpha}\right)^3$$

$$f_2 = 1 - \left(1 - \frac{2\alpha}{1 + 2\alpha}\right)^3$$

$$f_3 = f_2 \text{ (at } \alpha \leq \beta) ; \ f_3 = \left(\frac{1 + 2\beta}{1 + 2\alpha}\right)^3 - \left(\frac{1}{1 + 2\alpha}\right)^3 \text{ (at } \alpha > \beta)$$

The volume fractions of all the phases can be calculated varying the thickness of the Li$_3$TiO$_3$ phase, $l$, (or the parameter $\alpha$) from zero to infinity at the fixed value of the interface thickness $\lambda$ (or the parameter $\beta$). Mass fractions of the phases can be calculated using relations:

$$w_1 = \frac{\rho_1 f_1}{\rho_1 f_1 + \rho_2 f_2} ; \ w = \frac{\rho_2 f_2}{\rho_1 f_1 + \rho_2 f_2} ; \ w_3 = \frac{\rho_2 f_3}{\rho_1 f_1 + \rho_2 f_2}$$

where $p_1$ and $p_2$ are densities of the LTO and Li$_3$TiO$_3$, respectively; $w$ is the density of the interface phase is supposed to be similar to one for Li$_2$TiO$_3$ phase. The theoretical value of the charge-discharge capacity may be represented in the equation:

$$Q_{th} = (1-w)Q_0^0 + (w-w_3)Q_0^2 + w_3 Q_0^3$$

where $Q_0^0$ is the theoretical value for pure interface phase of Li$_2$TiO$_3$. Equation (13) differs from Equation (8) by the presence of the additional term $w_3 Q_0^3$, corresponding to the contribution of the interfaces (formally regarded as the interface phase) to the overall capacity of the material. In first approximation as a highest limit for the $Q_0^0$ value, one can assume that during charge/discharge this interface phase of Li$_2$TiO$_3$ may be converted into the limiting composition of Li$_3$TiO$_3$ corresponding to the specific charge/discharge capacity of 244 mAh g$^{-1}$, remaining electrochemically inactive outside the interface region. From the values $L = 500$ nm or 60 nm, $p_1 = 3.4$ g cm$^{-3}$; $p_2 = 4.0$ g cm$^{-3}$ and assuming that $\lambda = 6$ nm and $Q_0^3 = 244$ mAh g$^{-1}$, one can obtain theoretical dependences $Q_{th} = f(w)$, Equation (13), for the LTC composites with maxima qualitatively describing experimental values. It is clear that at low concentrations both theoretical and experimental data exceed the values predicted by Equation (8) and correspond to an upper limit of capacitance for ordinary mixture of the components. Figure 6 also shows that decrease in the grain size of LTO should lead to an increase in the capacitance and the shift of the capacitance maximum to the higher concentration of Li$_2$TiO$_3$ in the composites. This is the tendency for the composites obtained earlier by electro-spinning method with the LTO grain size of 60 nm [23]. In general, the model provides a rather good fit at low concentrations of Li$_3$TiO$_3$, whereas at high $w$ experimental capacity values decrease, possibly, due to diffusion limitations.

Besides high capacity, LTC composites at low concentration of Li$_2$TiO$_3$ have a better cycling rate and stability compared to LTO as shown in Figure 6a. This effect is caused by the higher ionic conductivity of the composites, as demonstrated in the impedance measurements above. Due to a strong difference in crystal structures of LTO and TiO$_2$, no strong interface interaction takes place in LTT composites. As a result, no additional increase in the electrochemical capacity and much less decrease in the grain boundary resistance is observed in these composites. At high concentration of Li$_2$TiO$_3$ the grain boundary resistance becomes high again and it leads to the decrease in the capacity as mentioned above.

No effect of the capacity enhancement is observed in LTT composites even at low concentration of the TiO$_2$ dopant. The reason appears to be negligible contribution of interfaces to the overall capacity of the composite. This fact may be explained by weak
interface interaction between LTO and TiO₂ due to a strong structure discrepancy between the phases.

5. Conclusions

Samples of pure Li₄Ti₅O₁₂ (LTO) with stoichiometric ratio of Li:Ti = 4:5 and composites LTO-Li₂TiO₃ (LTC) and LTO-TiO₂ (LTT) with excess amount of Li (Li:Ti > 4:5) and deficient in Li (Li:Ti < 4:5), respectively, can be prepared and investigated by X-ray diffraction, impedance spectroscopy and electrochemical charge-discharge techniques. This study shows that introduction of electrochemically inactive dielectric materials Li₂TiO₃ and TiO₂ to lithium titanium oxide LTO results in two non-trivial interrelated effects:

(i) A strong decrease in the grain boundary resistance of LTC composites at low concentration of Li₂TiO₃. The effect may be caused by easy formation of coherent interfaces between structurally similar phases Li₂TiO₃ and LTO leading to redistribution of lithium ions in the vicinity of the interfaces. With the increase of the concentration of Li₂TiO₃ in LTC composites, the grain boundary resistance goes through a minimum and increases again due to growth insulation layer of small Li₂TiO₃ particles around LTO grains. For LTT composites, a similar effect was observed, albeit not as strong.

(ii) Unusually high charge–discharge capacity of LTC composites at a low concentration of electrochemically inactive phase Li₂TiO₃ exceeding the theoretical value for pure LTO. This effect is likely to be caused by the appearance of the electrochemical activity of Li₂TiO₃ in the composite. This effect results from the interface interaction between LTO and Li₂TiO₃ taking place due to formation of coherent interfaces between structurally similar phases. The increase in the capacity may be qualitatively described in terms of a two-phase composite model with the interface layer of a high capacity. In addition, LTC composites have a better cycling rate and stability compared to LTO. This effect is caused by a higher ionic conductivity of the composites, as demonstrated in the impedance measurements above. Due to a noticeable difference in crystal structures of LTO and TiO₂, no strong interface interaction occurs in LTT composites.

Both effects are closely interrelated, and their primary reason seems to be the influence of interfaces on the physical properties of the components of the composite, namely, on its transport properties and the electrochemical capacitance. This should be common and may be observed in different composite electrode materials containing components with similar crystal structures.

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