The core-shell morphology study is crucial for composite materials, comprised of a low conductive core with a highly conductive thin carbon shell. The study analyzed carbon morphology evolution for the two series of Li4Ti5O12/C samples with carbon content increasing from 0.9 to 5.6 wt%. The conventional X-Ray Photoelectron Spectroscopy (XPS) study allowed us to conclude about the efficiency threshold of carbon layer growth over lithium titanate core for two carbon deposition methods – both sucrose and acetylene decompositions. Although the carbon layer thickness is increasing with carbon concentration growth in LTO/C composites, the efficiency of carbon coverage was shown to decrease with the threshold carbon concentrations about 1–2%. The chemical bonding analysis based on the same XPS data was used for C@LTO interface characterization. The proposed approach can be used for optimization of producing different composites with core-shell structure (carbon-based composites, materials with protective layers, and materials with gradient core-shell structure).

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Carbon-based composites are rather popular objects for investigation in materials science. In rechargeable lithium batteries, for example, different forms of carbon materials (CM) are used as a conductive additive to active electrode materials (EM) with relatively low electronic conductivity, namely LiFePO4 (lithium iron phosphate, LFP) with olivine structure,1–3 spinel-type LiMn2O4 (lithium manganese oxide, LMO),4,5 and spinel-type Li4Ti5O12 (lithium titanium oxide, LTO).4,7–9 Formation of through conductive network together with decreasing contact resistance between the two particles of EM increase overall conductivity of the composites and enable proper charge-discharge rates. Among the three materials mentioned above, LMO can boast of the highest electronic conductivity about $10^{-6}$ S·cm$^{-1}$,10 LFP with lower conductivity (about $10^{-9}$ S·cm$^{-1}$)10 reveals a stronger need in conductive additives. LTO with the lowest electronic conductivity (about $10^{-12}$ S·cm$^{-1}$)11 seems to be an ideal candidate for studying carbon-based composites used in lithium batteries.

Carbon content (Cc) in carbon-based composites demonstrates clear trend of decreasing from up to 7% in the earliest works11 through 5% down to below 3% in commercial products nowadays (see, for example),14 From one hand, Cc decreasing allows increasing the specific capacity. From the other hand, Cc decreasing can change the carbon-based composite geometry. CM and EM mixture with CM aggregate sizes dispersion is more typical for higher Cc values (Fig. 1a). The core-shell structure with carbon coating over EM core (Fig. 1c) is often associated with lower Cc. It should be stressed that only uniform core-shell geometry (Fig. 1c) allows significant decreasing of carbon additive fraction without breaking down through conductive network and increasing contact point resistance (Fig. 1b).

The carbon additive distribution study is obviously of the great importance for industrial manufacturing of LTO/C composite electrodes.15 The main idea of this work is the carbon layer morphology characterization for two series of the powder LTO/C composites. Particles, constituting these samples, have initially the same LTO core and two kinds of carbon shells. Such LTO/C composite diversity made possible the study of carbon shell morphology variation both between the samples with two carbon deposition methods and within series of samples with different carbon content.

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Carbon layer deposition.—Carbon coating was deposited by two diverse methods: both sucrose and acetylene decompositions in situ. In the well-known method of sucrose decomposition,16,17 lithium titanate was treated with different sucrose contents; then, the samples were annealed in the pure argon media at a temperature of about 750 °C for 8 hours. Tersely sucrose after melting and through a few intermediate stages decomposed into water vapors and carbon, which was deposited on the surface of LTO particles (referred to hereinafter as LTO/C5 composites).

In the second method, alumina boat with thin layer of LTO powder was blown by diluted acetylene (93% argon and 7% acetylene in the gas mixture) during different treatment time intervals (from 30 minutes to 8 hours) at 750 °C, which produced carbon layers on the surface of submicron LTO particles (LTO/C6 composites). This proprietary carbon coating method18 can be abbreviated as CGD (Chemical Gas Deposition) like the well-known Chemical Vapor Deposition method (CVD).

Both LTO/C5 and LTO/C6 series consisted of five samples with different carbon contents (Cc), adjusted by the content of decomposing sucrose (resultant Cc = 0.9, 1.3, 1.5, 2.8, and 5.6 wt%) and by synthesis time for acetylene decomposition (Cc = 0.9, 1.0, 1.2, 2.2, and 4.2 wt%).

Carbon layer characterization.—LTO/C surface compositional analysis was performed by X-ray Photoelectron Spectroscopy (XPS) using K-Alpha+ (Thermo Scientific, UK), with Al Kz monochromator (1486.6 eV). The analyzing beam diameter was 400 μm. The pressure in the analysis chamber was about 5 10−7 Pa. All the spectra were corrected with respect to the binding energy value of C 1s peak at 284.8 eV. In order to avoid surface layer damage, all the XPS measurements were made for as-synthesized powders without any sample treatment procedures.

The carbon content in LTO/C composites was determined by thermogravimetric analysis (TGA) using SETSYS Evolution TG/DSC (Setaram, USA). Measurements were carried out from room temperature to 770 °C in the atmosphere comprised of oxygen and argon mixture (1:4 vol.); so, the carbon content was defined by mass decrease during its oxidation.

The electrical conductivity of LTO/C composites was measured with porosity correction14 using a self-made two-contact cell with copper flat electrodes in a vacuum media. During the procedure, powder “as sintered” samples (without milling) were compacted under the 107 Pa pressure in order to avoid the damage of both LTO particles and its carbon layer. After calculation of the pore fraction, impedance spectroscopy method was used to determine the samples’ conductivity. Frequency dependence of the resistance was measured by the Solartron Analytical 1280Z Electrochemical Test System (Ametek, US) for every sample in the frequency range 0.01-2000 Hz); as a result, 2 Hz was chosen as the reference frequency.

Results and Discussion

LTO/C5 and LTO/C6 series comparison by XPS.—XPS as a method probing surface layer about 1–10 nanometers in depth was widely used for interface characterization in both pristine LTO20–22 and LTO/C composites.23–26 In our study, the comparison of Li 1s, C 1s, Ti 2p, and O 1s core line spectra for two series of LTO/C composites revealed notable difference of XPS spectra (Figures 2a and 2b). For the LTO/C5 series (Figure 2a), the carbon concentration growth (0.9 → 1.3 → 1.5 → 2.8 → 5.6%) leads to increasing of C 1s spectrum intensity and decreasing of Li 1s, Ti 2p, and O 1s spectra intensities. In the case of LTO/C6 series, the carbon content increasing is almost the same (0.9 → 1.0 → 1.2 → 2.2 → 4.2%), but intensity change is more pronounced (Figure 2b).

Such a distinction can be explained in terms of different composite types for LTO/C5 and LTO/C6 series. We can assume that sucrose decomposition is a less effective method for uniform carbon shell formation and resulting LTO/C5 composite geometry can be attributed to non-uniform carbon shells (Figure 1b) or even mixture-type (Figure 1a). Non-uniform carbon layers with some “open windows” lead to a less pronounced core band signal decreasing with Cc growth (Figures 2a and 2c). Acetylene decomposition can be considered as a more effective method of uniform carbon shells formation (Figure 1c). In this case, the Cc growth results in a more pronounced core band signal decreasing (Figures 2b and 2d).

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Figure 2. Core bands of XPS spectra for (a) LTO/C5 series, (b) LTO/C6 series, and the corresponding visualization of XPS in-depth probing for (c) non-uniform and (d) uniform carbon shells. Arrows lengths in (a) and (b) correspond to intensity changes, arrows directions – to carbon content increasing.

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XPS data interpretation in terms of coverage efficiency of carbon layer.—Both carbon coating non-uniformity and complicated surface morphology of particulate samples hamper quantitative characterization of carbon shell thickness by XPS data analysis. Nevertheless, a kind of semi-quantitative comparison of two different methods of carbon deposition can be done. In the Figure 3 one can see that the decreasing of Li/C, Ti/C, and O/C atomic ratios with carbon content increasing can be rather properly divides into two (“fast” and “slow” decreasing) regions. This two-region peculiarity is observed for Li/C(CC), Ti/C(CC), and O/C(CC) functions plotted both in linear (Figs. 3a, 3b) and logarithmic (Figs. 3c, 3d) scales.

From one hand, we cannot directly attribute these Li/C(CC), Ti/C(CC), and O/C(CC) functions or its derivative (slopes) to some method results in more uniform shell formation, the less effective one can be somehow attributed to carbon deposition methods. Such a peculiarity allows concluding about two distinctive stages (“fast” and “slow”) of carbon layer formation with clear threshold of carbon concentration. In frames of such an explanation of Figure 3 peculiarity, the growing carbon shell is more uniform at low carbon concentrations (stage I) and becomes less uniform at carbon concentrations above some threshold concentration Cth (stage II). The fact that threshold behavior is observed for both methods of carbon deposition, allows us to suppose the such a peculiarity can be common for various types of carbon-coated composites with low concentrations of carbon. The obtained threshold values Cth for LTO/C5 and LTO/C6 series lies in the range 1–2% (please keep in mind that XPS is semi-quantitative method). However, the slope values, proposed to be associated with carbon shell growth uniformity, differ drastically. At the first “fast” stage, acetylene decomposition results in about twice more uniform carbon shell, but for the second “slow” stage – up to six times more uniform.

Regarding to linear or logarithmic scales usage we can mention two reasons for choosing the latter one. The first reason originates from the fact, that in some cases the geometry of phase transitions can be described by Kolmogorov-Avrami formula.28,29 The similar double-slope curve in log-linear scale, was observed, for example, for the time dependences of XRD and scattered light intensities, measured during PZT films annealing.30 Two slopes correspond to two (fast and slow) stages and describes so-called “geometrical catastrophe” of crystallization kinetics. We cannot use Kolmogorov-Avrami formula directly because the studied process is not phase transition, but in case of almost the same volume of XPS probed surface such a comparison with phase transition is not so contradicting. From this point of view, the growing phase (carbon) displace the initial phase (LTO) and the geometry of this kinetics depends on carbon deposition method. The fact, that the carbon concentration for LTO/C5 series is a function of heating time and we can redraw Figs. 3b, 3d as time dependences, makes the proposed comparison even more reasonable.

The second reasons of using logarithmic scale is based on our experience in the characterization of self-similar objects (for example, surfaces17 or clusters)31 and self-organized processes (for example, domain wall motion in ferroelectrics).32 The powder surface itself can be easily considered as fractal objects with scaling behavior. Scaling is usually described by power laws thus resulting in different dependences, linear in log-log plots (see, for example).31 In the Figure 3 we use only linear-linear and log-linear scales, because the proper fractal analysis require large enough scaling region. Maybe in the following studies with wider range of carbon concentrations we or someone else will be able to analyze the scaling behavior of carbon deposition.

In any case, the threshold behavior of Li/C(CC), Ti/C(CC), and O/C(CC) functions is observed regardless to scale type usage. In this work, we compare these functions for two series of LTO/C composites, reveal the threshold behavior, propose the explanation in terms of coverage efficiency of carbon layer, and, finally, assume that this finding will be valuable for industrial applications. The deeper understanding of its fundamental origins will require further studies (both theoretical and experimental) as for carbon-based composites, so for others core-shell compounds.

Results validation by other methods.—The carbon additive in LTO/C composites is responsible for throughout electronic conductivity, so conductivity measurements (Fig. 4) should be considered
as a principal validation method. Two LTO/C$^\text{S}$ and LTO/C$^\text{A}$ series comparison at Figure 4 confirms made above conclusion about more effective carbon coverage by acetylene decomposition method. The electronic conductivity in LTO/C$^\text{A}$ series grows faster with carbon concentration increasing and reaches $2.3 \cdot 10^{-3}$ S/cm at a lower carbon concentration (about 1.2 wt%). The similar value of electronic conductivity in LTO/C$^\text{S}$ series is obtained at three time higher carbon concentration (about 4.5 wt%).

The assumption about the threshold behavior of carbon deposition also does not contradict to electronic conductivity data. It’s clearly seen that conductivity grows faster at the first stage ($C_\text{C} < C_\text{th}$) and slower at the second ($C_\text{C} > C_\text{th}$). Nevertheless, we should mention that the presented results do not directly validate threshold behavior. It’s not surprising, keeping in mind that the Li/C, Ti/C, and O/C atomic ratios are supposed to be semi-quantitative parameters, specific to one given method – XPS. It’s clear that it somehow correlates with core-shell morphology, and core-shell morphology also somehow correlates with throughout electronic conductivity. But we have no reason to expect linear correlation of Li/C, Ti/C, and O/C atomic ratios and electronic conductivity. Moreover, in case of LTO/C$^\text{S}$ series the coverage efficiency reaches its threshold and became less effective at $C_\text{C} = 1.5$ wt%, but such a concentration is still not enough for proper throughout conductivity and $C_\text{C}$ should be increased further to about 3 wt% or even 4.5 wt% (depending on desired C-rate, for example). Such a difference between carbon coverage efficiency (Figures 2 and 3) and electronic conductivity (Figure 4) correlates with band positions of all core bands (Li 1s, C 1s, Ti 2p and O 1s). One can see the small, but notable shifts of all core bands for $C_\text{C} = 0.9$, 1.3 and 1.5 wt% for LTO/C$^\text{S}$ series (Figure 2a) and $C_\text{C} = 0.9$ and 1.0 wt% for LTO/C$^\text{A}$ series (Figure 2b). Such a small shift (about 0.5 eV) is often attributed to insufficient surface conductivity, so this specific to XPS conductivity occurs in LTO/C$^\text{S}$ series at the lower carbon content comparing with LTO/C$^\text{S}$ series (1.2 and 2.8 wt% correspondingly). Also we suppose that the obtained critical concentration $C_\text{th}$ cannot be directly attribute to percolation threshold (see, for example,38). We can assume only that the percolation threshold differs for LTO/C$^\text{S}$ and LTO/C$^\text{A}$ series and lie in the range 1±3 wt%, as concluded in Ref. 34.

High-resolution transmission electron microscopy (HRTEM) is another popular method of carbon layer characterization, but it can be hardly used in this work. First of all, the particle sizes in studied low-C composites is hundreds nanometers, while the carbon layer thickness – few nanometers and maybe even less. Such a proportion makes HRTEM study challenging (and makes alternative methods of the increased importance). Also such a proportion of particle size/carbon layer thickness usually doesn’t allow studying carbon shell uniformity at the whole particle scale. Usually HRTEM images shows only one segment of the core-shell particle (see, for example, recent35 for sucrose decomposition or36 for acetylene decomposition). Moreover, the methods can visualize the very thin “belt” of carbon layer in-between upper or lower halves of the particle.

**Chemical bonding analysis.**—Besides morphological study, XPS can be also used for C@LTO interface characterization by chemical bonding analysis. For all the examined samples, C 1s band was decomposed into five peaks (Figure 5). Please mention that we used symmetric shape of C 1s peaks. Such a simplified fitting is more common in electrochemical society, but could be not fully correct for quantitative characterization of C 1s peak fractions. The C 1s band for samples with high concentration of sp$^3$ carbon will have a broad, asymmetric tail toward higher binding energy. The at the Figure 5 we use symmetric shape of C/C=C=C peak instead of asymmetric one due to three main reasons.

First, the obtained electric conductivity data corresponds to more amorphous phase with low fraction of sp$^3$ carbon. Second, the most part of publications about LTO/C (as well as LFP/C) sample, prepared with different methods of carbon deposition demonstrate Raman spectra with significant (even dominating) fraction of disordered and sp$^3$ carbons. Third, we don’t use asymmetric shape of the fitting peak because its proper application will require throughout study of carbon
The evolution of three C 1s core band components with carbon content increasing. Comparison of XPS data for (a) LTO/C^S (left column) and (b) LTO/C^A composites.

Layer disordering in LTO/C composites using, for example, Raman spectroscopy (RS). Without such a standalone RS study we are not able for choose proper fitting parameters, especially keeping in mind, that sp^3/sp^2 ratio can vary with carbon concentration growth and differs for LTO/C^S and LTO/C^A series. Since we don’t have enough data for proper usage of asymmetric shape of C-C/C=O peak, we use a symmetric one. Such a simplified fitting is a clear approximation, so further we will use only qualitative, but not quantitative interpretation of C 1s band deconvolution data.

Coming back to Figure 5, the resulted five C 1s peaks can be attributed to C=O (284.5 eV), C-O (285.5 eV), C=O (286.9 eV), O=C=O (289.2 eV) and CO_3^{2-} (290.5 eV) bonds as proposed in Refs. 23, 41–45. Dedryvere et al. propose the similar interpretation of two main differences – the presence of additional peaks between C=C/C=O and C-O, and above 291 eV. Whereas these peaks were attributed to CH_2 and CF_2-like carbon atoms of PVDF, correspondingly, for our binder-free samples we can exclude them. However, we have to mention about another possible interpretation of the fifth C 1s peak, we use a simplified interpretation of peak near 291 eV in terms of CO_3^{2-} (or sp^3 π shakeup transitions) inputs evolution with carbon concentration growth. The C=C/C=O and C-O inputs vary significantly – at the Figure 5 one can see the lowest fraction of C-O peaks and even the C-C/C=O peaks intensity decreasing due to screening by growing carbon shell (graphene oxide) with lower amount of C-O bonds. This second explanation is partially confirmed by non-linear dependence of C-C/C=O and C-O peaks intensities on carbon concentration, similar to core LTO peaks intensity decreasing due to screening by growing carbon shells (Figure 4). We think that both explanations of C-O peak origin are correct and should be used jointly (at least for sucrose decomposition).

The analysis of data, shown in Figure 6, can also help with an interpretation of the fifth C 1s peak, located between 290-291 eV. First, we can hardly expect a notable amount of residual Li_2CO_3, resulting in CO_3^{2-} detection. Second, even if some amount of Li_2CO_3 would exist on the LTO surface, it should be effectively screened by growing carbon shell, similar to decreasing of core LTO bands (Figure 4). In our study, this relatively standalone peak remains notable and steady for all carbon concentrations (Figure 6), the slight variation of atomic % can be attributed mentioned low accuracy of quantitative characterization of the conductive carbon layer. So, the direct comparison of C=C/C=O, C-O and this fifth peaks proves the version of π* ← π shakeup transitions. Such an interpretation of the peak origin is important because of demonstrated correlation between peak area with carbon additive conductivity. The steady fraction of π* ← π peak in C 1s band for different Cc values can indicate that overall electrical conductivity of LTO/C composites (Figure 3) is defined mainly by carbon shell morphology, but not its structure. In this case, the uniformity of highly conductive carbon shell, provided through a conductive network even for low Cc values, is more important than the structural characterization with ordered/disordered carbon fraction estimation.

Conclusions

In this research, we studied two series of LTO/C composites with different carbon contents. Carbon layers with increasing thickness were deposited over Li_4Ti_5O_12 core particles by sucrose and acetylene decompositions. The C@LTO surface study by conventional XPS allowed us to conclude about the threshold coverage efficiency of carbon layer for both deposition methods. The shell formation can be described as more effective below some threshold carbon concentration C_b, and becomes much less effective above it. The C_b values for average LTO particle sizes about 300 nm were defined as 1÷2 wt% for both sucrose and acetylene decomposition. Acetylene decomposition was shown to be more effective method for uniform carbon shell formation, so can be proposed to be preferable synthesis method for LTO/C composites with low carbon concentration. Sucrose decomposition results in less uniform carbon layer formation. The optimized working window for carbon additive in LTO/C composites are about 0.5÷2.5 wt% and 1÷5 wt% for acetylene and sucrose decompositions correspondingly.

The C 1s band analysis of the same experimental results allowed us to propose the strong bonding formation between carbon from shell and oxygen from LTO core, as well as the presence of π* ← π shakeup transitions. The interpretation of peak near 291 eV in terms of π-π bonding (or π electrons) is proposed to be an alternative to the popular interpretation in terms of CO_3^{2-} bonding.

We want to stress that the shown difference of two carbon deposition methods and revealed threshold behavior of carbon layer formation is just one more step toward deeper understanding of interfacial processes in composite electrode materials. The next step is to use these findings for more detailed interpretation of the electrochemical data. Also, we hope that proposed methods of LTO/C composites characterization will be used as a simple and effective tool of composite parameters optimization for different electrode materials with core-shell structure.

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