Efficiency Threshold of Carbon Layer Growth in Li$_4$Ti$_5$O$_{12}$/C Composites

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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 Li$_4$Ti$_5$O$_{12}$/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 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/C8 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/C8 and LTO/C5 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 Kα 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 correction11 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 105 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/C8 series comparison by XPS.**—XPS as a method probing surface layer about 1–10 nanometers in depth19 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/C8 series, the carbon content increasing is almost the same (0.9→1.9→2.9→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/C8 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).

![Figure 2. Core bands of XPS spectra for (a) LTO/C5 series, (b) LTO/C8 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.](image-url)
Ti/C(CC), and O/C(CC) functions or its derivative (slopes) to some (Figs. 3a, 3b) and logarithmic (Figs.3c, 3d) scales. Method results in more uniform shell formation, the less effective coverage efficiency over LTO core. In these terms, the more effective characterizing the decreasing rate, can be somehow attributed to carbon deposition can be done. In the Figure3 one can see that the function 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 divided 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 definite physical or chemical property of LTO/C. XPS itself is semi-quantitative (not truly quantitative) method of chemical composition characterization. Moreover, we should keep in mind the asymmetric nature of C 1s spectrum due to metal-like conductivity of carbon layer.27 Such a property of conductive carbon additive also hampers quantitative interpretation, so we further will focus on qualitative and semi-quantitative description.

From the other hand, we study surface morphology of LTO/C composites and XPS is semi-quantitative, but trustable tool for surface layer characterization. We cannot claim that Li/C(CC), Ti/C(CC), and O/C(CC) functions have clear physical or chemical meanings, but if they will help us to characterize the surface morphology change for LTO/C composites with consistently growing carbon concentration, it will prove its utility. Let’s assume that Li/C(CC), Ti/C(CC), and O/C(CC) slopes, characterizing the decreasing rate, can be somehow attributed to carbon coverage efficiency over LTO core. In these terms, the more effective method results in more uniform shell formation, the less effective one – in less uniform. At the same carbon concentration Cc, a non-uniform carbon shell should result in the higher values of core lines intensities, comparing with uniform shells (Figures 2c and 2d, correspondingly). Uniform carbon coverage (Figure 2d) effectively screens the core LTO particle thus resulting in pronounced decreasing of Li 1s, Ti 2p and O 1s core band intensities (Figure 2b). Less uniform carbon coverage (Figure 2c) leaves some open windows or areas with thinner carbon layers, thus resulting in small decreasing of core bands intensity.

The most intriguing and valuable result of this study is the two-slopes form of Li/C(CC), Ti/C(CC), and O/C(CC) dependencies, observed for both 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/C8 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 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.29 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, surfaces30 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).33 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\textsuperscript{a} and LTO/C\textsuperscript{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\textsuperscript{A} series grows faster with carbon concentration increasing and reaches 2.3 \times 10^{-3} \text{ S/cm} at a lower carbon concentration (about 1.2 wt\%). The similar value of electronic conductivity in LTO/C\textsuperscript{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\textsuperscript{S} series the coverage efficiency reaches its threshold and became less effective at C_\text{C} = 1.5 \text{ 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\textsuperscript{S} series (Figure 2a) and C_\text{C} = 0.9 and 1.0 wt\% for LTO/C\textsuperscript{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\textsuperscript{S} series at the lower carbon content comparing with LTO/C\textsuperscript{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, 87). We can assume only that the percolation threshold differs for LTO/C\textsuperscript{S} and LTO/C\textsuperscript{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 in-depth analysis – few nanometers and maybe even less). Therefore, we can conclude that result validation by HRTEM images analysis is senseless in this work, because single or few images can neither prove nor disprove “statistical” results, obtained by XPS. We can only hope that we or some other team will have enough resources to perform big-data HRTEM study for the understanding the fundamental origins of the revealed threshold behavior of carbon layer deposition.

We believe that the approach described above can be used for finding out the threshold behavior (if any) in different composites with core-shell structures. We can mention not only carbon-based composites (LTO/C, LFP/C, LMO/C, etc.). It can be used also for electrode materials with protective layers, preventing SEI formation and undesirable ion dissolutions, 37, 38 materials with gradient core-shell structure, 39 and other surface-modified materials. Also such an approach can be used for study of the electrode material degradation, induced by ion dissolution and/or undesirable structural transformations during cycling. 40

**Chemical bonding analysis.**—Besides morphological study, XPS can be also used for C\text@LTO interface characterization by chemical bonding analysis. For all the examined samples, C1s band was decomposed into five peaks (Figure 5). Please mention that we used symmetric shapes 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 C1s band for samples with high concentration of sp\textsuperscript{2} carbon will have a broad, asymmetric tail toward higher binding energy. At the the Figure 5 we use symmetric shape of C/C=\text{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\textsuperscript{2} 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\textsuperscript{3} carbons. Third, we don’t use asymmetric shape of the fitting peak because its proper application will require throughout study of carbon

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**Figure 4.** Electrical conductivity for (a) LTO/C\textsuperscript{S} and (b) LTO/C\textsuperscript{A} composites.

**Figure 5.** The C1s core band deconvolution into five peaks for LTO/C\textsuperscript{S} composite with C_\text{C} = 2.8%. Second, single HRTEM image will study the morphology of the only particle (or even its part). The quantitate description of carbon shell morphology by HRTEM is possible, but it will require proper statistics – tens or hundreds of images. In our case of two set of samples with five carbon concentration each, the study will require thousands of HRTEM images. Unlike HRTEM, the unique property of XPS as a characterization tool is a combination of thin surface layer probing (less than 10 nm in Z direction) and averaging over millions of particles (analyzing beam diameter was 400 \mu m, while the average particle size was about 0.3 \mu m). Therefore, we can conclude that result validation by HRTEM images analysis is senseless in this work, because single or few images can neither prove nor disprove “statistical” results, obtained by XPS. We can only hope that we or some other team will have enough resources to perform big-data HRTEM study for the understanding the fundamental origins of the revealed threshold behavior of carbon layer deposition.
layer disordering in LTO/C composites using, for example, Raman spectroscopy (RS). Without such a standalone RS study we are not able to choose proper fitting parameters, especially keeping in mind, that sp²/spⁿ ratio can vary with carbon concentration growth and differs for LTO/C⁵ and LTO/C⁴ series. Since we don’t have enough data for proper usage of asymmetric shape of C-C/C=C peak, we use 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-C/C=C (284.5 eV), C-O (285.5 eV), C≡O (286.9 eV), O=C=O (289.2 eV), and CO₃²⁻ (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≡C=O and C-O, and above 291 eV. Whereas these peaks were attributed to CH₂- and CF₂-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, located between 290-291 eV. First, the analysis of data, shown in Figure 6, can also help with an in-depth explanation of C-O peak origin. The second explanation is based on the supposition that some part of C-O bonds measured by XPS can be attributed to the strong bonding between carbon shell and core oxygen from Li₁₄Ti₅O₁₂. In this case, the C-O peak decreasing is explained 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≡C 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 Li₂CO₃, resulting in CO₃²⁻ detection. Second, even if some amount of Li₂CO₃ 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=C, 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.46 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 Li₁₄Ti₅O₁₂ 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 Cₚ, and becomes much less effective above it. The Cₚ 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 decomposi-

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Figure 6. The evolution of three C1s core band components with carbon content increasing. Comparison of XPS data for (a) LTO/C⁵ (left column) and (b) LTO/C⁴ composites.

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