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## **Citrate-Derived Carbon Nanocoatings for Poorly Conducting Cathode**

### A Detailed Study Using TiO<sub>2</sub> Substrate Materials

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Preparation of conductive coatings is an effective way for improvement of kinetics in Li battery materials. Although carbon-based conductive coatings are most often used, they have been studied less systematically than, for example, phosphides or phosphocarbides. In this study we tried to find the most important correlations between the preparation conditions and the resulting composition, morphology, and electrical properties of selected carbon-coated materials. As a model substrate material we mainly used TiO<sub>2</sub> particles while as a carbon precursor we employed citric acid. For comparison, other substrates and precursors were occasionally used. It is shown that in the typical temperature range between 500 and 800°C, the carbon yield varies from 3 to 10 wt %, depending on the initial heating rate and on the duration of heat-treatment. Correlations between the composition, morphology, and the conductivity of final composites are thoroughly discussed. The steep increase in conductivity beyond the percolation threshold (between 1–2 wt % of carbon) can be correlated with the occurrence of a uniform, 1–5 nm thick carbon film that appears to be continuous on a micrometer scale. Finally, we show that the activation energies for conduction in various carbon-coated samples (0.04–0.13 eV) are strikingly similar to those found previously for phosphide- or phosphocarbide-based coatings and even for LiFePO<sub>4</sub> doped with supervalent ions.

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Many materials for positive battery electrodes with interesting thermodynamic properties (high voltage, high theoretical capacity) are by nature typical ceramic materials with quite low electronic conductivity ranging from about  $10^{-3}$  S cm<sup>-1</sup> for LiCoO<sub>2</sub> down to  $10^{-9}$  S cm<sup>-1</sup> for LiFePO<sub>4</sub> at room temperature.<sup>1-5</sup> To enhance the insertion/deinsertion kinetics of such materials it is necessary to create an efficient electron-conducting network among or around the active particles. For active materials from the upper part of the conductivity range  $(10^{-3}-10^{-5} \text{ S cm}^{-1})$  it is usually sufficient to create percolated conduction pathways by adding a sufficient amount (several wt %) of an electron conductor (typically carbon-based) in the form of fine powder (Fig. 1a). To achieve a comparable performance with the poorest conductors (e.g.,  $LiFePO_4$ ), the presence of a simple percolated conducting network seems to be insufficient. It has been shown empirically<sup>6-9</sup> and theoretically<sup>10,11</sup> that the overall transport in electrodes based on poorly conductive active particles is only fast enough if an electron conductor surrounds the whole surface of each particle (typical particle size of practical materials is in the order of 100 nm). Obviously, the conductive coatings (Fig. 1b) help create a close-to-optimal wiring situation where the mixed transport of electrons and lithium ions proceeds more or less spherically into/out of active particles. Here it should be stressed that, in fact, the impact of electron conducting coatings on the ionic transport remains rather unclear. One can speculate that the coatings are thin enough (they are reported to be in the order of 1 nm or even less<sup>9</sup>) that ions can penetrate through them without significant polarization. Alternatively, ions could penetrate through defects in the structure of coatings. In any case, it has been shown experimentally that thicker coatings (with average thickness 2-3 nm or more) do show a deteriorating effect on the electrochemical kinetics,9 probably reflecting a hindrance of the ionic transport in such cases.

Although the general picture concerning the role of conducting coatings presented above might seem quite consistent, various alternative views may be found in literature, especially when considering specific practical cases. For example, Chung et al.<sup>5</sup> reported that the excellent electron conductivity of LiFePO<sub>4</sub> doped with selected supervalent ions was due to changes in the electronic structure of these materials with respect to the electronic structure of poorly conductive pristine LiFePO<sub>4</sub>. Later on, Ravet et al.<sup>12</sup> rejected this possibil-

ity, claiming that in those materials the reason for conductivity enhancement was the presence of a percolated conducting network consisting of elementary carbon. Another explanation for conductivity enhancement in certain LiFePO<sub>4</sub>-based materials refers to the presence of small amounts of phosphides or phosphocarbides which are known for their metallic-like conducting properties.<sup>5</sup> In some cases, in which authors do attribute the conductivity enhancement to the presence of carbon, they assume that carbon is present in the form of a dispersed nanophase rather than in the form of coatings.<sup>13</sup> Finally, we have shown in our own reports<sup>9,14,15</sup> that certain preparation procedures result in architectures where the active substance does not appear in a particulate form but rather in a form of porous monoliths. Although there are indications that the carbon formed in this procedure is deposited on all surfaces of such a material in the form of a ca. 1 nm thick coating, we have not been able to prove this general picture unambiguously.

The present study is a first attempt to find clear correlations between the preparation conditions and the resulting composition,



Figure 1. Schematic presentation of two limiting types of cathode composites consisting of poorly conductive electrochemically active particles and a second, well-conductive phase: (a) The case where the well-conductive phase forms percolating pathways within the composite. Although the average conductivity of such a composite may be very high, the electrochemical (insertion) reaction is very fast only at selected places on a particle's surface, that is, where the conducting phase is in electronic contact with the substrate particles. (b) The case where the conductive phase forms a coating around each active particle. The coating must be permeable for the reacting ions (the permeability is indicated by the cracks in the layer although permeation may be realized via an arbitrary mechanism). Here the insertion reaction is equally fast at all points on the particle's surface.

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morphology, and electrical properties of selected carbon-coated composites. To avoid the influence of substrate on electrical conductivity measurements, we chose among insulators with a conductivity less than  $10^{-10}$  S cm<sup>-1</sup>. At the same time we wanted the substrate to have a uniform size to allow for easier and more reproducible study of morphological and electrical features of prepared composites. For the purpose of generality, it was also desirable that the substrate was available in different particle sizes, ranging from micro- to nanometer range. A material that satisfied these criteria was TiO<sub>2</sub> (mainly in the anatase modification). Still, to rule out completely a possible influence of the substrate composition and morphology on selected properties of interest, we occasionally also used other substrates (LiFePO<sub>4</sub>, flat quartz). As a carbon precursor, we mostly used the citrate anion. Namely, as we have shown in a range of previous papers,<sup>9,14,15</sup> this precursor yielded uniform films on LiFePO<sub>4</sub>, the thickness of which could even be tuned. To study the aforementioned correlations, the following preparation conditions were controlled and changed in a systematic way: (i) the composition of the initial dispersion containing the substrate and organic precursor, (ii) the homogeneity of the initial dispersion, (iii) the heating rate, (iv) the final heating temperature, and (v) the duration of heat-treatment. The resulting materials composition was studied using mainly thermogravimetric (TG) analysis partly supplemented with X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDS) analysis, the morphological features were studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and the electrical conductivity measurements were performed using impedance spectroscopy. To find the conduction mechanism in various composites, temperature dependence of the samples' conductivity was measured and commented on with respect to selected previous results.

### **Experimental**

As substrate particles for preparation of carbon coatings, three different sets of TiO<sub>2</sub> particles were used. The most extensive studies were performed using anatase particles "Riedel-de Haen 14027" which, according to the producer, have a mean particle size value of 0.25 µm. For comparison, 1 µm Aldrich 248576-100G and 25-70 nm Aldrich 634662-25G TiO2 particles were used. The respective specific surface areas of these particles determined in our laboratory using a Brunauer, Emmett, and Teller (BET) analysis (Micromeritics TriStar 3000) were: 9.6, 9.0, and 20  $m^2\ g^{-1}.$  In one experiment, the carbon films were additionally prepared on a flat quartz plate and on a LiFePO<sub>4</sub> cathode material for Li batteries. In the latter case, we used a special sol-gel procedure<sup>9,14,15</sup> in which in the carbon precursor (citrate) and the material's precursors were mixed on the molecular level and both the LiFePO4 and carbon phases were created and separated later on, during the heating procedure. In the case of TiO<sub>2</sub> particles, carbon films were prepared by adding a known amount of the particles into an aqueous solution of citric acid. The mass ratio between TiO<sub>2</sub> particles and citric acid was varied in a wide range to obtain the final composites containing a carbon content from 0 to more than 20 wt % (for comparison, pure citric acid was also used in one experiment). The resulting dispersion was first homogenized using an ultrasound mixer, dried, and finally heat-treated according to a selected procedure. In one experiment, solid citric acid and substrate TiO<sub>2</sub> particles in appropriate mass ratio were simply ground together and the obtained solid mixtures were heat-treated according to a specified procedure. In the case of the flat quartz substrate, we used for the carbon precursor naproxen instead of citric acid. It appeared that upon heat-treatment, naproxen formed more uniform carbon films on the flat quartz surface which, later on, gave more reproducible conductivity measurements. Naproxen was simply melted on the substrate surface and then burnt according to a specified thermal procedure in inert atmosphere.

If not specified otherwise, the samples were heat-treated in a gas-tight quartz tube with a moderate but constant flow of Ar 5.0. The initial heating rate was  $10^{\circ}$ C min<sup>-1</sup>. After reaching the prese-



Figure 2. TG curves for  $TiO_2$  (0.25  $\mu$ m)–carbon composites with different initial contents of citric acid (as indicated beside the curves).

lected temperature, the samples were further heated for 10 h at that temperature and then left to cool down to room temperature.

After the heat-treatment, the carbon content in all composites (except in the sample with flat quartz substrate) was determined using TG analysis. The measurements were performed on a Mettler Toledo TGA/SDTA 851° thermoanalyzer in a temperature range from 30 up to 650°C at a heating rate of  $10^{\circ}$ C min<sup>-1</sup>. The TG curves were recorded in an oxygen flow of 100 mL min<sup>-1</sup>. The initial mass of samples was approximately 50 mg. In all cases, the baseline was subtracted.

The morphology of prepared composites was investigated using a field-emission SEM—Supra 35 VP Carl Zeiss. For selected samples EDS analysis was also performed. Selected powdered material were spread on holey carbon-coated Cu grid and investigated by a high-resolution field-emission TEM JEOL 2010F.

The X-ray powder diffraction pattern of the samples was collected on a Philips PW 1710 diffractometer using Cu K $\alpha$ 1 radiation ( $\lambda = 1,5418$  Å). The data were collected in the range between 15 and 70°20 in steps of 0.04°.

For conductivity measurements, the obtained composite powders were pressed in pellets using about 10 wt % of Teflon as a binder. The diameter of pellets was always 8 mm while the thickness varied from 1.75 to 2.65 mm. The contacts were made by painting both basal planes using either a silver conductive paste (for room-temperature measurements) or a Pt paste (for measurements of conductivity as a function of temperature). The room-temperature impedance measurements were performed in air conditions while the temperature-dependent impedance spectra were recorded by putting the sample in a gas-tight quartz tube equipped with appropriate shielded Pt wires and thermocouples. Prior to and during heating, an inert atmosphere was maintained within the tube using a 5.0 Ar. The impedance spectra were recorded in a frequency range of 1 MHz to 20 Hz with a Hewlet Packard 4284A instrument.

#### **Results and Discussion**

Influence of synthesis parameters on carbon yield.— The first series of samples was prepared by heat-treating the initial mixtures containing a different precursor (citric acid): substrate (0.25  $\mu$ m anatase) ratios. In all cases the heating regime was the same: the initial heating rate was 10°C/min while after reaching the final temperature of 900°C the samples were maintained at that temperature for 10 h. TG curves for these samples recorded in oxygen atmosphere are shown in Fig. 2. In all cases it was assumed that the carbon content was proportional to the weight loss between 300 and 600°C, respectively. A comparison between the initial materials composition (established through precise weighting of reactants) and the composition of final composite shows that the carbon yield is more or less independent of the content of citric acid in the initial



**Figure 3.** Carbon yield as a function of precursor (citric acid)-substrate mass ratio for (a) different substrate particles and for different methods of composite preparation and (b) for different initial heating rates (i.e., heating rates before reaching the final carbonization temperature of 900°C).

dispersion (Fig. 3a) and amounts on average  $3.4 \pm 0.5\%$ . One of the reasons for the comparatively low yield is the fact that citric acid contains oxygen atoms. Indeed, it has been reported that the yield can be maximized by maximizing the ratio between the content of aromatic fragments and the content of heteroatoms.<sup>16</sup> When slightly larger TiO<sub>2</sub> particles were used  $(1 \ \mu m)$ , the yield remained similar but dropped to only about 2.3% if 70 nm particles were employed (Fig. 3a). The reason for this decrease is not clear. More expected is the decrease observed in samples where the initial mixture was less homogeneous, i.e., prepared by simple "dry mixing" of solid reactants rather than dissolving or dispersing and mixing them in appropriate solvents (Fig. 3a, full triangles). We believe that in such less homogeneous samples a larger portion of organic precursor is detached from the substrate during heating (probably carried away by the large amount of gases evolved during carbonization) and deposited elsewhere in the heating chamber. In a way, this assumption is consistent with the next set of experiments in which the initial heating rate was gradually decreased from 10 to 1°C/min (Fig. 3b). Apparently, with lower heating rates, the process of carbonization becomes less vigorous, that is, it involves lower rates of gas evolution, which results in smaller losses of solid carbonized material.

Anomalies due to interaction between carbon precursor and substrate during carbonization.— One of the crucial parameters affecting the process of carbonization is expected to be the plateau value of carbonization temperature. Figure 4a shows that the yield remains quite constant within the range 500–750°C but then starts to decrease significantly, especially above 900°C. At 960°C the carbon yield is only about 2%. Based on several supplementary tests we assume that this low yield can be a consequence of at least three



**Figure 4.** (a) Carbon yield as a function of carbonization temperature. (b) TG curves for the composite samples prepared at different carbonization temperature; only the sample prepared at 960°C exhibits an increase in mass above ca. 500°C.

different processes taking place at high temperatures. The first is indicated already in the TG curve for the sample prepared at 960°C, which shows an increase in mass between 500 and 650°C (Fig. 4b). This increase is attributed to changes in the substrate (TiO<sub>2</sub>) rather than changes in the organic precursor. Indeed, XRD patterns of untreated TiO<sub>2</sub>-citric acid sample and two samples treated at 960°C for different periods of time show important structural changes in the substrate (Fig. 5). Apart from the expected partial transformation from anatase to rutile,  $^{17,18}$  the diffractogram at 960°C (10 h) also shows the presence of Ti<sub>9</sub>O<sub>17</sub>. It is assumed that during subsequent recording of TG curves (in oxygen), this phase is transformed back into TiO<sub>2</sub>, hence the observed increase in mass. The second, and, as shown later, important reason for understanding the conductivity measurements, may be the low carbon content determined for the high-temperature samples could be entrapment of a significant amount of carbon into agglomerates. To confirm the possibility of such an entrapment, we additionally heat-treated a sample prepared at 900°C and a sample prepared at 960°C for 1 h at 800°C in air conditions. While the former sample turned into a whitish nuance typical for carbon-free TiO<sub>2</sub>, the latter retained a brown-grayish hue indicating the remainders of carbon within the sample, similar to that reported previously for carbon coatings on  $Al_2O_3$ .<sup>19</sup> The presence of carbon in this sample was additionally confirmed using an EDS analysis before and after the additional heat-treatment (not shown). This result implies that the sample prepared at 960°C contains a higher total content of carbon than observed with TG and displayed in Fig. 4a. We take advantage of this implication when explaining an anomaly observed in conductivity measurements (c.f.,



**Figure 5.** XRD patterns for three selected samples prepared using the 0.25  $\mu$ m TiO<sub>2</sub> substrate particles: (bottom) uncarbonized sample containing citric acid, (middle) sample carbonized at 960°C for 1 h, and (top) sample carbonized at 960°C for 10 h. The peaks pertaining to different phases are marked as explained in the legend.

Fig. 9 and the corresponding discussion). A third reason for the low carbon yield at 960°C could be due to further carbonization processes expected at higher temperatures.

Another effect observed in TiO<sub>2</sub> substrate, which can be attributed to the presence of carbonized phase, is a decrease in the rate of anatase  $\rightarrow$  rutile transformation. The XRD diffractogram in Fig. 6a shows that in the case of 70 nm TiO<sub>2</sub> particles, already the untreated sample contained a mixture of anatase and rutile phases in an approximate ratio of 3:1. As expected, upon heat-treatment an additional amount of anatase transformed into rutile. However, at equal heating conditions, the sample containing more carbonized phase (ca. 1%) retained a larger portion of anatase structure than the one with the smaller (0.31%) carbon content (see Fig. 6b and c, respectively). This result is consistent with several earlier reports on the role of carbon in anatase  $\rightarrow$  rutile transformation.<sup>20-23</sup> The traces of unidentified phase in Fig. 6b and c could be related to a reduced TiO<sub>2</sub> phase, similar to that discussed earlier (c.f., Fig. 5 and the corresponding explanation in text).

Morphology of  $TiO_2$ -carbon composites.— The effect of carbonization on materials' morphology was studied using SEM (Fig. 7 and 8) and TEM (Fig. 9). First it should be noted that the typical particle size of as-received sample designated by the producer as "0.25  $\mu$ m



**Figure 6.** XRD patterns for three selected samples prepared using the 70 nm  $\text{TiO}_2$  substrate particles: (bottom) initial  $\text{TiO}_2$  substrate particles, (middle) carbonized sample with 0.99 wt % of carbon, and (top) carbonized sample with 0.31 wt % of carbon. The peaks pertaining to different phases are marked as explained in the legend.



Figure 7. SEM micrographs of selected carbonized samples prepared with 0.25  $\mu$ m TiO<sub>2</sub> particles: (a) untreated TiO<sub>2</sub> particles, (b) carbon content <0.02%, (c) carbon content=0.80%, (d) carbon content=2.66%, (e) carbon content=4.42%, and (f) carbon content=20.53%.

particles" was significantly smaller (<200 nm) than the nominal value. This smaller value is consistent with the "average particle size" that can be evaluated from BET measurements: taking the measured value of specific surface area  $(9.6 \text{ m}^2 \text{ g}^{-1})$  and the theoretical density for anatase  $(3.82 \text{ g cm}^{-3})$ , one gets for average particle size a value of ca. 160 nm (if assumed that the particles are spherical). In carbonized composites (Fig. 7b-e) containing low carbon contents, the carbon phase cannot be observed as a separate morphological feature. We assume that at low contents the carbon phase is rather homogeneously (uniformly) distributed around and between the substrate particles. The typical dimensions of carbon phase (either thickness, if a film, or radius, if aggregates) should be less than ca. 5–10 nm (i.e., less than the resolution of SEM at present conditions). A good uniformity on a scale from ca. 1 to



Figure 8. EDS line analysis of the sample prepared with 0.25  $\mu m$  TiO\_2 and containing 3.62 wt % of carbon.



**Figure 9.** TEM micrographs of carbon-TiO<sub>2</sub> composites: (a,b) examples of two different morphologies found in sample with 0.80 wt % of carbon; (c,d) two typical morphologies found in sample with 2.66 wt . % of carbon. The crystal planes of TiO<sub>2</sub> can be clearly distinguished from the more disordered and transparent surface film and patches due to carbon.

ca. 100  $\mu$ m was indirectly confirmed by performing EDS analysis on selected samples. A typical concentration profile for carbon obtained by EDS line scan is shown in Fig. 8. It can be seen that along a line of ca. 50  $\mu$ m in length, carbon is distributed quite uniformly, that is, it forms a continuous path, although its concentration fluctuates on a micrometer scale. The continuity of carbon on these scales is very important for understanding why good electrical behavior can be achieved already at relatively low carbon content (see next section).

TEM micrographs (Fig. 9) reveal the carbon distribution on a nanometer scale. It seems that at very low carbon contents (up to ca. 1 wt %) the substrate surface is mostly carbon-free (Fig. 9a). A thorough inspection, however, reveals the presence of isolated carbon patches at certain spots (Fig. 9b). Based on a large number of inspections, the general impression is that, at low concentrations (below ca. 1 wt %), carbon tends to agglomerate at selected spots rather than spread over the entire substrate surface to form films. Such films, however, are clearly observed at concentrations above ca. 2 wt % (Fig. 9c). Although a major part of carbon now deposits in the form of a quite uniform film, it should be stressed that larger agglomerates (patches) can still be observed (Fig. 9d). A similar morphology development was observed in our previous studies where carbon coatings were prepared on LiFePO4.9,15 It can be expected that the transition from the mostly carbon-free surface at ca. 1 wt % of carbon to the uniformly carbon-covered surface at ca. 2 wt % of carbon will lead to a corresponding transition in electrical properties, i.e., the conductivity percolation threshold should lie between 1 and 2 wt % of carbon.

Another well-seen feature in Fig. 7 is the decreasing average particle size with increasing carbon content. This is consistent with some previously published results<sup>22,23</sup> in which authors reported that the presence of carbon phase prevented sintering of particles during heat-treatment. Analogous trends in sample morphology to those shown in Fig. 7 were observed for the 70 nm particles (not shown).

Impact of carbon phase on the electrical properties of composites.- The main feature of the impedance spectra of pellets prepared from different TiO<sub>2</sub>-carbon composites was an arc, or at high carbon contents a part of an arc, in complex plane. It is reasonable to attribute such an arc to a parallel combination of a capacitance due to bulk dielectric properties of the pellet and a resistor due to average resistivity (or, alternatively, average conductivity) of this pellet. The average pellet conductivity as a function of carbon content for differently prepared TiO<sub>2</sub>-carbon composites is displayed in Fig. 10. The basic curve (Fig. 10a) obtained for the most investigated 0.25  $\mu$ m anatase sample shows a typical percolation shape<sup>24</sup> with a roughly estimated percolation threshold between 1-2 wt % (in good agreement with TEM observations, see the previous section). The maximum (plateau) conductivity of composites is between 0.1 and 1.0 S cm<sup>-1</sup>, a value commonly obtained for insulators or poor conductors doped with carbon.<sup>24</sup> For battery purposes, the materials slightly above the percolation threshold are the most interesting: there the best compromise between the requirement of high enough a conductivity (e.g. >0.01 S cm<sup>-1</sup>) and as low as possible a carbon content (i.e., to avoid unnecessary decrease of energy density) is achieved. In the present case, the samples with about 2.5 wt % of carbon could represent such a compromise. Decreasing the heating rate moderately improves the conductivity at a given carbon content (Fig. 10b). Based on this, and on some previously shown results (see Fig. 3 and the corresponding discussion), we speculate that a less vigorous carbonization process with a lower rate of gas evolution can result in a slightly more uniform carbon distribution on the surface of substrate particles and/or between them.

Knowing the basic percolation curves, we were interested in how conductivity develops if a selected composite with a given starting precursor content is heated to different final temperatures. The results in Fig. 10c show that heating up to 500°C gives a very poor conductivity of the composite (comparable to the conductivity of pure  $TiO_2$ ). This indicates that up to this temperature no conducting carbon phase has been developed. By heating to higher temperatures, the conductivity improves significantly. Such an increase in conductivity above 500°C has been observed previously for other carbon materials.<sup>24</sup> At 700°C the carbon phase achieves a maximum conductivity (within the conditions tested in the present study). Heating to higher temperatures decreases the carbon content, consistent with the results shown in Fig. 4a. Very interestingly, this loss of carbon shifts the conductivity points exactly along the percolation curve obtained in a completely different way (see discussion of Fig. 10a). In other words, it seems that, at least for samples prepared between ca. 700 and 900°C, the conductivity of the composites is determined mainly by the carbon content but is quite insensitive to the preparation procedure. This result can be explained by a good uniformity of the composites. The only exception is the point at 960°C. Based on the previous results, especially those shown in Fig. 4 and 7, we explain this significant deviation by at least three possible effects: (i) the carbon content for this point is not determined correctly (due to possible carbon entrapment within sintered agglomerates, see explanations for Fig. 4a and 7b), (ii) the conductivity of the carbon phase is further increased due to a possible further process of carbonization/graphitization (see discussion on the deviation of the point at 960°C in Fig. 4a), and (*iii*) the conductivity of substrate itself is significantly increased, thus contributing to the total composite conductivity. The last mechanism refers to formation of a reduced TiO<sub>2</sub> phase, for example, such as observed in Fig. 5, and to literature data which show that reduced TiO<sub>2</sub> phases may exhibit metallic properties.25

We also checked the possible impact of the substrate size on composite conductivity (Fig. 10d). While the larger particles with similar sizes (0.25 and 1  $\mu$ m) show similar conductivities, the smaller particles (70 nm) exhibit somewhat higher conductivities at a given carbon content. The reason for this effect is unclear. In principle, it could be related to the incorrect determination of carbon content using TG, as a consequence of carbon entrapment into ag-



Figure 10. Conductivity as a function of carbon content for different samples prepared in this study: (a) A basic curve obtained with the samples containing the 0.25 µm TiO<sub>2</sub> substrate particles and carbonized at 900°C for 10 h with the initial heating rate of 10°C/min; average values of up to 10 individual measurements are shown as points, and the bars represent standard deviations. (b) The effect of initial heating rate on the final conductivity of selected composites. (c) The effect of carbonization temperature; the samples denoted by triangles were obtained by carbonizing a set of equal initial samples with given precursor content at different carbonization temperatures. (d) The effect of particle size and the preparation method on the conductivity of final composites.

glomerates (see Fig. 4a). We hoped that a more detailed analysis of the percolation curves for different samples could give additional information in this respect. For analysis we took the frequently used,<sup>26,27</sup> though simplified,<sup>28</sup> scaling equation which is only appropriate for phenomenological description of the percolation curve at the volume fractions of conductive phase, *p*, higher than the percolation threshold,  $p_c$ 

$$\sigma = \sigma_0 \left( \frac{p - p_c}{1 - p_c} \right)^t$$
[1]

where  $\sigma$  is the sample conductivity,  $\sigma_0$  is the bulk conductivity of the conducting phase, and *t* is an exponent related to dimensionality of the conducting network.<sup>26,27</sup>

Analyzing the measured percolation curves using Eq. 1, one finds that, unfortunately, uncertainty of parameters determination is too high to make a conclusive comparison between different samples. It can, however, be generally concluded that the maximum value of conductivity of the carbonized phase itself (ca. 100 S cm<sup>-1</sup>) is much lower than the maximum conductivity of graphite (26,000 S cm<sup>-1</sup> along the a-axis in single-crystalline graphite, 1300 S cm<sup>-1</sup> for polycrystalline graphite).<sup>29,24</sup> The value of percolation threshold varies quite a lot but it is safe to claim that it does not exceed 4 vol % (about 2 wt %). The dimensionality factor, *t*, also shows large variations. The most reliable results were obtained for the 0.25  $\mu$ m TiO<sub>2</sub> (*t* = 1.9 ± 02). This indicates that the carbon phase is more or less isotropically distributed within the composite. Namely, the theoretical value of *t* for ideal 3D networks of conductive phase is reported to be 1.94, while for 2D structures this value is 1.3.<sup>26,27</sup>

In the last set of experiments we measured the activation energy for electron conduction in selected carbonized composites (Fig. 11). The results for the 0.25  $\mu$ m TiO<sub>2</sub>-carbon system are compared with a system of high interest for battery research, namely LiFePO<sub>4</sub> decorated with a carbon coating.<sup>9-11,14,15</sup> Most importantly, the carbon coating on LiFePO<sub>4</sub> was prepared using the same precursor as used throughout the present study, the citric acid. To check for the generality of these curves, we prepared two further samples. One was a carbon-coated LiFePO<sub>4</sub> material where, as the carbon precursor, a mixture of citric acid and gelatine was used. The last sample was a carbon-coated flat quartz substrate where the coating was prepared by heat-treatment of naproxen. Despite the big differences in the selected systems, one can observe several common features in the measured Arrhenius plots in Fig. 11. The most important is that all systems exhibit a gradual increase in activation energy with increasing temperature but, also, similar values of the slopes at lower temperatures. This type of Arrhenius curve has been previously reported for amorphous and partly graphitized carbons<sup>30</sup> and has been attrib-



Figure 11. Arrhenius plots for different samples measured in inert atmosphere in temperature range 25–500°C.

uted to a wide distribution of barrier heights and widths at sp<sup>2</sup> sites. A larger degree of graphitization (e.g., due to different heattreatment or a different substrate) can bring about weaker temperature dependence and, hence, a smaller average slope.<sup>30</sup> This means that most differences in the observed curves can be explained by the slightly different degree of graphitization of these samples. Having this in mind, we find it quite remarkable that the difference between the highest (0.13 eV) and the lowest (0.04 eV) activation energy observed for these systems is relatively small. In any case, this brief analysis and comparison with literature data indicates, with a high probability, that the electron conduction in all these systems is primarily determined by the carbon phase and is essentially independent of the substrate and even of the precursor type. Although such a conclusion might seem quite obvious in the present context, it should be reminded that authors often seek for alternative explanations. As mentioned in the introduction, the best-known example is the dispute between Chung et al.<sup>4</sup> and Ravet et al.<sup>12</sup> about the nature of electron conduction in doped LiFePO<sub>4</sub> materials. Comparing the present data with those published by Chung et al.,<sup>4</sup> one may find it very indicative that the activation energies for the materials prepared by Chung et al. (0.062–0.075 eV, see Ref. 4) lie in the middle of the range determined for the present materials (0.04-0.13 eV) and that the room temperature values are of the same order of magnitude  $(0.01 \text{ S cm}^{-1})$ . The values of activation energies determined by Herle et al.<sup>5</sup> for various iron phosphates (0.03–04 eV) are also similar to the ones determined in Fig. 11. Of course, a mere comparison of activation energies is insufficient for reliable determination of a conduction mechanism. However, given the present results and their comparison with literature data, one should consider the possibility that in all these materials, which may contain various interesting phases, the phase which determines the overall conductivity is always the carbon phase.

#### Conclusions

Heat-treatment of citric acid in the presence of TiO<sub>2</sub> substrate particle leads to relatively low carbon yields (typically 3.4  $\pm$  0.5% after 10 h of heating at 900°C in Ar atmosphere). This relatively low yield is quite suitable for battery purposes where a compromise between the content of inactive material and the total conductivity is required. In any case, the yield can be increased up to 10%, if the initial heating rate is decreased from 10 to 1°C. Between 500 and 800°C the yield is independent of the heating temperature, but at higher temperatures it starts to decrease. Various mechanisms for this behavior are proposed. Above ca. 2 wt % the carbon phase forms more or less homogeneous coatings around the substrate particles, such as those observed in our previous work on olivines. Conductivity as a function of carbon content exhibits a typical percolation behavior with a percolation threshold of about 1-2 wt % and a conductivity plateau within the range of 0.1-1 S cm<sup>-1</sup>. Decreasing the heating rate moderately improves the conductivity at a given carbon content. To achieve a full conductivity of the carbonized phase, the composite material has to be treated at a temperature of at least 700°C. The Arrhenius plot for conductivity of the heattreated TiO<sub>2</sub>-citric acid sample shows a similar shape and a similar value for activation energy (0.04-0.13 eV) as a range of other materials prepared in the present study: LiFePO4-citrate, LiFePO4citrate + gelatine, and SiO<sub>2</sub>-naproxene. Interestingly, this is the same range as previously reported for various LiFePO<sub>4</sub>- based materials in which, however, the conduction was attributed to noncarbon phases.4,3

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