

Short communication

Morphology and electrical properties of conductive carbon coatings for cathode materials

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Available online 3 July 2007

Abstract

Many interesting cathode materials, such as LiFePO_4 , LiMnPO_4 , LiFeBO_3 or the recently discovered $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{MnSiO}_4$, exhibit extremely low electronic conductivity ($<10^{-9} \text{ S cm}^{-1}$). A very efficient way for improving the electronic transport in such materials is supposed to be the preparation of carbon coatings around individual active particles. Despite the increasing number of reports on preparation of various carbon coatings, neither the formation mechanism nor the detailed coating properties have been explained satisfactorily. The present paper is an attempt to find a clear correlation between the synthesis parameters, the resulting coating morphology and, finally, its electrical properties. As a substrate material for deposition of coatings, more or less monodisperse TiO_2 particles in various sizes were used. As a carbon precursor, citrate was used because it had given excellent results in our previous investigation of the LiFePO_4 system. It is shown that citrate precursor delivers pretty good conductivity (ca. 30 S cm^{-1}) after a 10 h heat treatment at 700°C or higher. The conductivity percolation threshold can be reached already at 1.5 vol.% of carbon, while the plateau conductivity of the whole composite is about 0.1 S cm^{-1} . At that level, the carbon phase is supposed to form a well-distributed 3D electrical network within the composite.

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Keywords: Electronic conductivity; Carbon coating; Percolation; Electrical properties; Li-ion batteries

1. Introduction

The most serious limitation of many advanced cathode materials is their poor electrical conductivity. To achieve fast enough transport in such materials, it is necessary to reduce the average length of solid-state diffusion to a few tens of nanometres or less. One possibility is to prepare nanopowders of active material where each nanoparticle is both electronically and ionically in contact with the respective reservoirs. It has been shown theoretically [1,2] that such contact is most efficient if prepared in the form of a coating with mixed conductive features. For example, the coating is essentially an electronic conductor that is also permeable to ions (Fig. 1). Various experimental reports strongly indicate that carbon coatings of appropriate thickness may possess such “mixed conducting” properties [3–6] which accounts for their successful application to LiFePO_4 .

While the crucial role of carbon coatings in improving the electrochemical performance of cathode materials seems to be undisputable, there remain many open questions concerning the correlation between coating morphology and the resulting composite electrode properties. Examples of such questions are (a) How much carbon is needed for formation of uniform coatings? (b) Is there a correlation between coating uniformity and conductivity? (c) What is the maximum composite conductivity that can be achieved with carbon coating? (d) Does substrate affect the coating properties, in particular its conductivity?

The present contribution tries to find answers to such questions. In the first part, we discuss the influence of preparation parameters (precursor ratio, heating rate, duration of heat treatment, etc.) on basic coating properties. As a substrate we used TiO_2 particles (mostly in anatase form). The reason for this selection is not only the fact that TiO_2 has recently received considerable attention as a potential battery material [7–9], but also because these particles are available as (more or less) monodisperse spheres of different dimensions, so the impact of substrate size could be studied as well.

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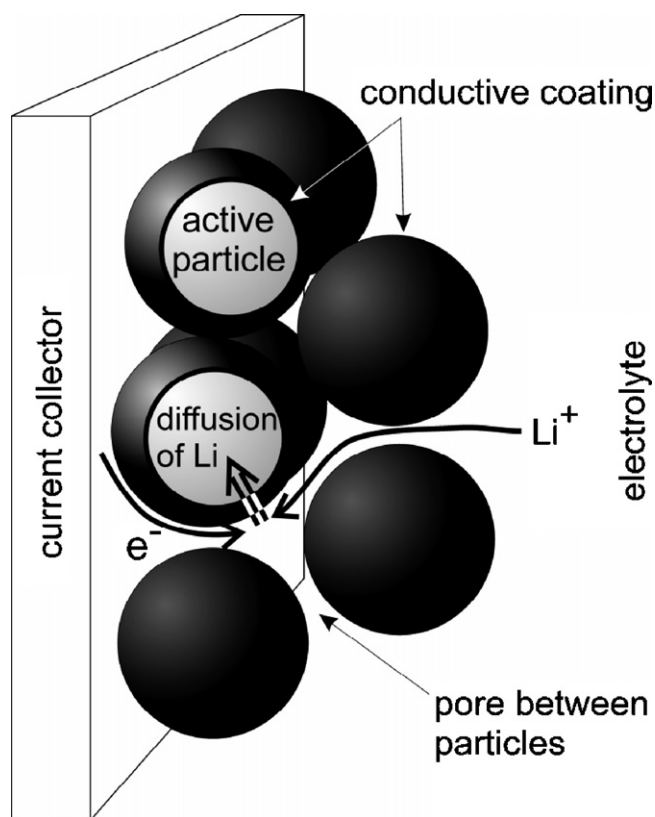


Fig. 1. Schematic presentation of electron and ion transport in a carbon-coated cathode material with poorly conductive active particles.

As the precursor for carbon coating formation, we are using citric acid because the carbonization process of this precursor is basically known from a number of our previous studies on other substrates, in particular LiFePO_4 [6,10,11]. In the second part, we study typical morphological features of prepared coatings. The third part is devoted to careful analysis of electrical properties of the obtained composites. Comments on the results are made with respect to the morphology and composition of the carbon–substrate composites.

2. Experimental

TiO_2 particles of three different sizes were used: anatase particles “Riedel-de Haen 14027” with a nominal mean particle size of $0.25 \mu\text{m}$, “Aldrich 248576-100G” with a nominal size of $1 \mu\text{m}$ and “Aldrich 634662-25G” with particle sizes between 25 and 70 nm. The respective specific surface areas were found to be: 9.6, 9.0 and $20 \text{m}^2 \text{g}^{-1}$. Carbon coatings on TiO_2 particles were prepared by adding different known amounts of the particles into respective aqueous solution of citric acid. The obtained dispersions were homogenized, dried and heat treated. Different heating regimes were used. After heat treatment, TiO_2 -carbon materials with different contents of carbon, approximately in the range from 0 to 20 wt.%, were obtained.

The samples were heat treated in a gas-tight quartz tube with a moderate but constant flow of Ar 5.0. In most cases, the initial

heating rate was $10^\circ\text{C min}^{-1}$. After reaching the pre-selected temperature, the samples were further heated for 10 h and then left to cool down to room temperature.

The carbon content was calculated from thermogravimetric data obtained using a Mettler Toledo TGA/SDTA 851^e thermoanalyzer. The TG curves were recorded in an oxygen flow of 100mL min^{-1} . The baseline was subtracted in all cases.

The morphology of prepared composites was investigated using a Field-Emission Scanning Electron Microscope—Supra 35 VP Carl Zeiss equipped with an EDS analyser and a high-resolution field-emission TEM Jeol 2010F.

The electrical properties of the prepared materials were measured on 8 mm diameter pellets containing about 10 wt.% of teflon as a binder. The typical thickness of pellets was about $2.0 \pm 0.5 \text{mm}$. The contacts on basic planes were made either using a silver or a Pt conductive paste. The impedance spectra were recorded in a frequency range of 1 MHz to 20 Hz with a Hewlett Packard 4284A instrument.

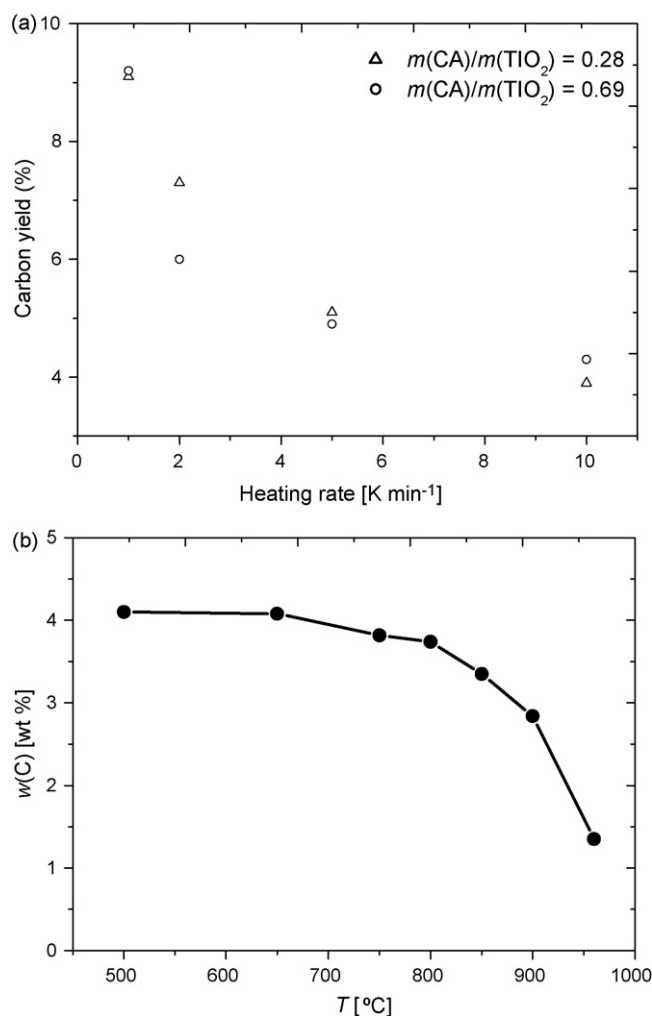


Fig. 2. The influence of (a) initial heating rate and (b) final heating temperature on the carbon yield. In all cases, the ratio between the mass of initial precursor (citric acid) and TiO_2 was the same: 0.687. The duration of heating at the final temperature was always 10 h.

3. Results and discussion

When preparing carbonized materials for use in batteries, one must find a balance between two contradictory requirements: a high enough carbon content to get sufficient electrode conductivity but low enough to preserve the high energy density of the electrode. Fig. 2 shows that the final carbon content is significantly influenced by the initial heating rate (Fig. 2a) but also by the final heating temperature (Fig. 2b). The rate of carbonization increases at higher heating rates: as the rate of carbonization reaction increases, gas evolution becomes more vigorous. The evolving gases carry significant amounts of surrounding material away from the reaction zone, more so as gas evolution becomes faster. Less expected is the significant influence of carbon content on the final heating temperature (Fig. 2b). There could be several reasons for this phenomenon, but we believe that there are probably only two that are predominant. The first explanation of this phenomenon is based on the fact that at higher temperatures, TiO_2 is transformed into Ti_9O_{17} or into a similar oxygen-deficient phase, as confirmed by X-ray diffraction (not shown). Upon subsequent recording of TG (in oxygen atmo-

sphere), the reduced phase is re-oxidized which results in an error in determination of the carbon content.

The second, and more important, reason was partial entrapment of carbon due to particle growth and agglomeration at higher temperatures. During subsequent TG measurements, the entrapped carbon could not be detected, so apparently a lower content than the actual content was determined. The assumption that a part of carbon is entrapped within agglomerates is consistent with conductivity measurements (see results and discussion below). In the conclusion, the results of Fig. 2 indicate that there should be a sort of “direct or indirect interaction” between the substrate and the carbon phase, at least at high enough temperatures. However, at 700°C (a “standard carbonization temperature”) it seems that such interactions still do not take place. This is indirectly confirmed by the fact that the carbon yield (the efficiency of conversion of precursor into carbon) is quite independent of the initial mass ratio between the active particle and carbon precursor, in our case citric acid (compare both curves in Fig. 2a where the final heating temperature was always 700°C). If there were interactions between carbon and substrate, one should expect different yields for each of the curves.

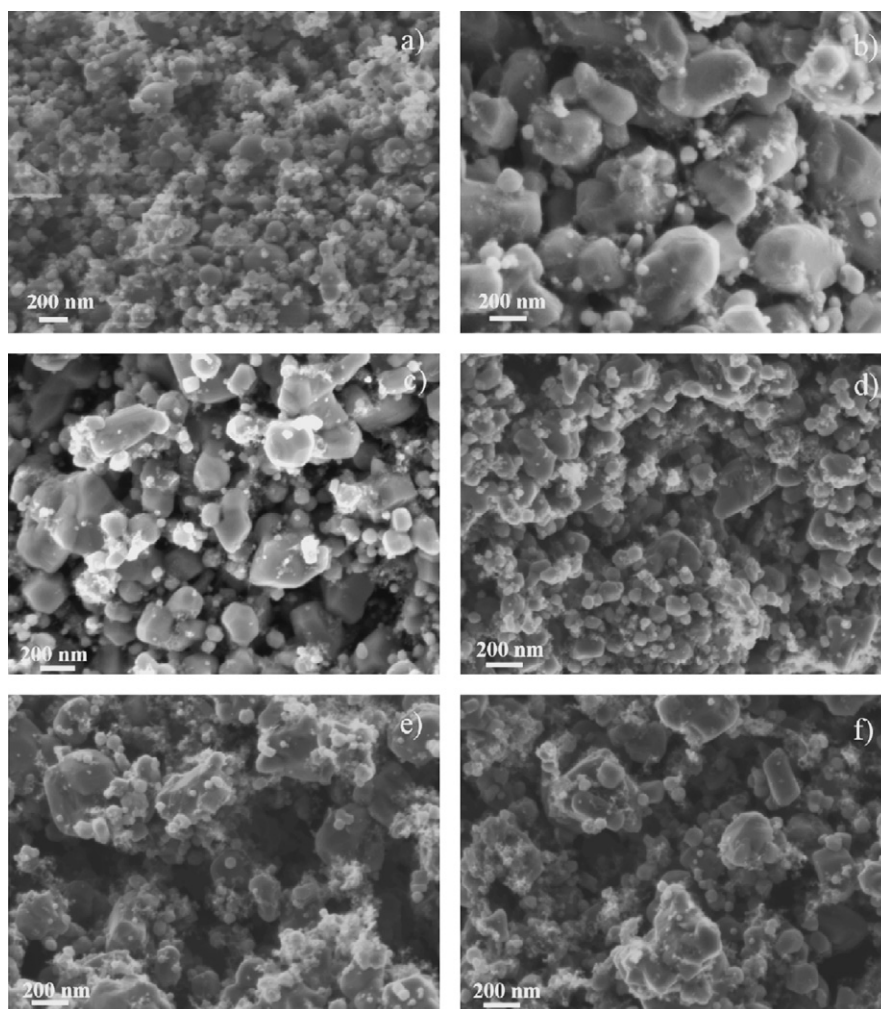


Fig. 3. SEM micrographs of selected carbonized samples prepared with 70 nm TiO_2 particles: (a) untreated TiO_2 particles, (b) carbon content $<0.02\%$, (c) carbon content = 0.80% , (d) carbon content = 2.66% , (e) carbon content = 4.42% and (f) carbon content = 20.53% .

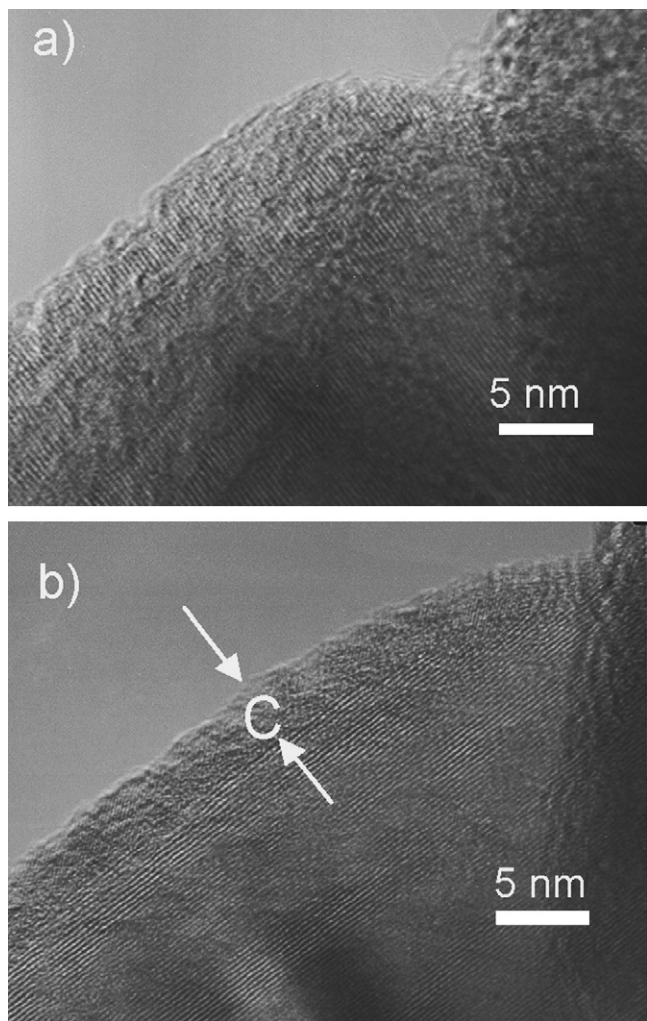


Fig. 4. TEM micrographs of carbon-TiO₂ composites: (a) example of a carbon-free surface at 0.80 wt.% of carbon and (b) example of uniform nanocoating at 2.66 wt.% of carbon. The crystal planes of TiO₂ can be distinguished from less ordered carbon film.

The morphology of obtained carbon–substrate composites is shown in Figs. 3 and 4. One clearly sees that thermal treatment (10 h at 700 °C) leads to considerable increase in average particle size, especially at low carbon content. Higher carbon content somewhat suppresses particle growth but the average particle size is still larger than in an untreated sample (Fig. 3a). In SEM micrographs, the carbon phase cannot be observed as a separate morphological feature. Obviously, carbon is not deposited in the form of larger agglomerates. TEM micrographs of composites with low carbon content (ca. <1.5 wt.%) show different situations on different surface spots: in many cases, a completely bare substrate surface can be observed (Fig. 4a), while in other cases, a carbon film with a typical thickness of several nanometres can be observed, as shown in Fig. 4b. The latter situation is regularly observed at carbon contents >2 wt.%. Apart from that, high carbon content leads to the formation of small carbon agglomerates (typical size <10 nm) at certain spots on the substrate surface (not shown). However, these agglomerates are still too small to be observed with ordinary SEM investigation, as displayed in Fig. 3. As a whole, one might conclude

that below ca. 1.5–2 wt.% there is not enough carbon to spread throughout the substrate particles. At higher contents, however, most particles are covered by a several nanometre-thick carbon film plus a certain amount of small carbon agglomerates. Based on such morphological developments, one can expect that the electrical properties will dramatically change in the region near 1.5–2 wt.% of carbon.

Indeed, the electrical measurements of a range of TiO₂–C materials containing different amounts of carbon confirmed the above anticipations. The specific conductivity displayed in Fig. 5 was calculated from the impedance spectra of corresponding TiO₂–C pellets with a well-defined thickness and known surface area (painted with a conductive Ag paint). A sharp increase in conductivity at carbon contents from ca. 1–2 wt.% can be observed, while plateau conductivity occurs above ca. 5 wt.% of carbon. For practical purposes an electronic conductivity of ca. 10^{−3} S cm^{−1} is usually sufficient. This conductivity is achieved at a carbon content of about 2 wt.%. The next crucial information for practical preparation of conductive carbon films concerns the minimum heating temperature necessary for satisfactory conductivity to occur. Development of conductivity with increasing temperature of heat treatment is shown in Fig. 5b. Note that

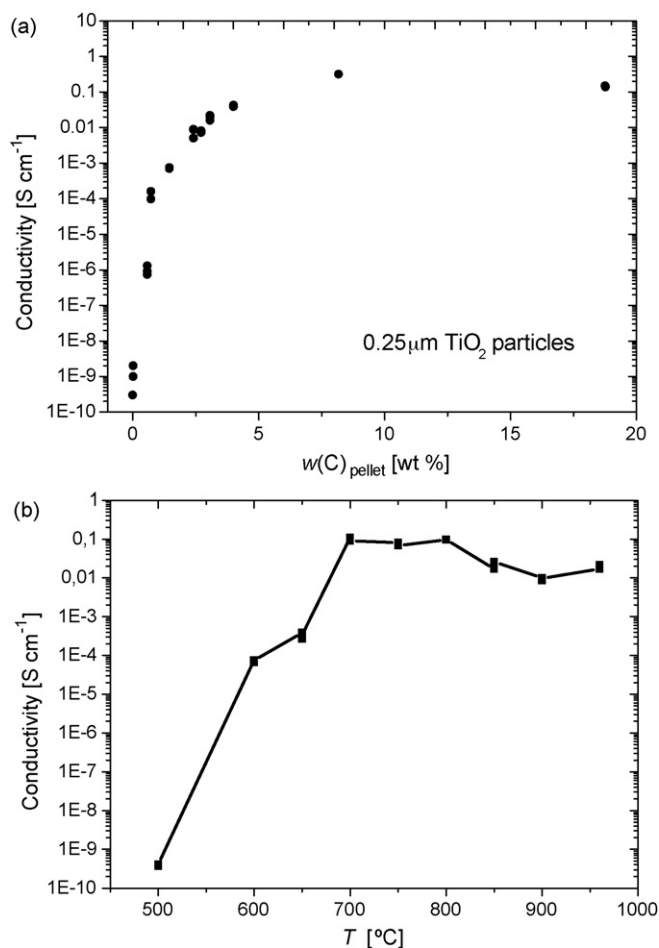


Fig. 5. (a) Conductivity as a function of carbon content for the 0.25 μm TiO₂ substrate particles. (b) Conductivity as a function of final heating temperature. In all cases, the samples were heated for 10 h at given temperatures.

each point corresponds to 10 h of treatment at that temperature. It is obvious that heating to about 500 °C (or less) is insufficient to convert citrate to conductive carbon. Above 500 °C the conversion to conductive carbon is more and more efficient, consistently with some previous investigations [12]. Heating above 700 °C does not increase the conductivity. On the contrary, even a slight decrease is observed in the range from 800 to 900 °C. This decrease can be related to loss of carbon for reasons discussed when explaining the results of Fig. 2 (see above).

In the next series of experiments, we varied the size of TiO₂ particles to find a possible correlation between the particle size and conductivity, keeping the conditions of carbonization constant. Three particle sizes were selected: 70 nm, 0.25 and 1 μm. In all cases, we obtained percolation curves similar to those displayed in Fig. 5a. To find a possible quantitative difference between samples, we fitted such curves using the classical scaling equation [13,14]

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

where σ is the sample conductivity, σ_0 the bulk conductivity of the conducting phase, p the volume fraction of conductive phase, p_c the percolation threshold and t is an exponent related to dimensionality of the conducting network [13,14]. In order to use Eq. (1) it is necessary first to transform mass fractions of carbon in composites into volume fractions. In our case this was not possible, as the density of the carbonized phase was unknown.

For this reason, we calculated the volume fractions using arbitrary values of densities within a range that appeared most reasonable. For example, as the upper value of density we simply took the theoretical density of graphite (2.25 g cm⁻³), while the lowest possible density was determined experimentally by measuring the density of differently prepared carbonized samples without the presence of TiO₂ substrate (1.2 g cm⁻³). The measured curves were then redrawn at many density values and each curve was fitted using Eq. (1). The results of this rather extensive fitting analysis are displayed in Fig. 6. There are many interesting pieces of information that can be extracted from Fig. 6. The first is the value of the bulk conductivity of the conducting phase itself (carbon), σ_0 . The average value of σ_0 for all three samples was about 30 S cm⁻¹, which is significantly lower than the value for pure polycrystalline graphite (1300 S cm⁻¹) [12,15]. As expected under present conditions, the carbonization process cannot yield graphite-like structures [16]. However, the partial graphitization that takes place above 500 °C is sufficient to provide acceptable conductivity for batteries. It is surprising that the average conductivity of carbon grown around the 70 nm TiO₂ particles is significantly lower (about 8 S cm⁻¹) than for the other two TiO₂ substrate particles (>30 S cm⁻¹). At present, the reason for this difference is unclear but the fact is that these particles have a higher specific surface area, which probably leads to a stronger interaction between the TiO₂ particles and carbon phase. Another feature that should be considered in future investigations of this effect is related to the structure of TiO₂. We found using X-ray diffraction that the 70 nm particles con-

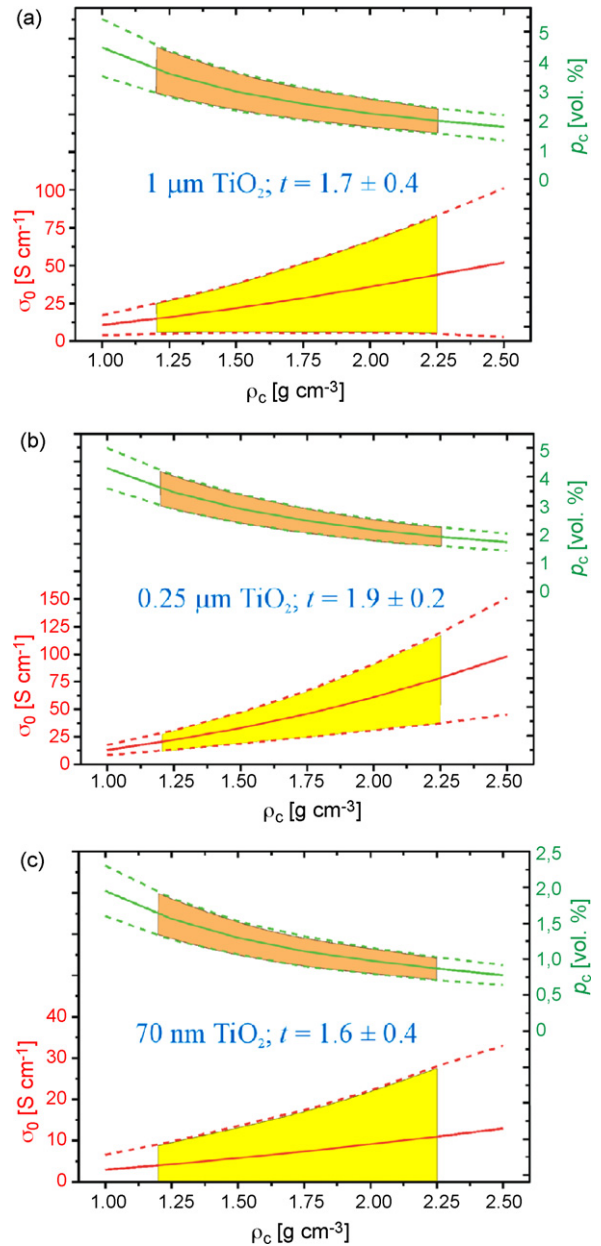


Fig. 6. Bulk conductivity of the conductive phase (σ_0) and percolation threshold (p_c) as functions of the density of conductive phase. Both quantities, as well as the exponent t , were determined by fitting the measured percolation curves (only the part above the percolation threshold) using Eq. (1). The width of the “bands” corresponds to the error of fit.

tained, beyond anatase, a significant amount of rutile [16]. The other two samples, however, consisted of pure anatase.

Different behaviour of the smallest (70 nm) TiO₂ particles is also reflected in the different percolation threshold, p_c (see the right ordinate axes in Fig. 6a–c). While the average percolation threshold for both larger TiO₂ particles is about 2.5 vol.%, the average p_c for the 70 nm is only 1.5 vol.%. For battery purposes, a lower percolation threshold is favoured because less carbon is needed to achieve the same conductivity of the composite electrode.

The last parameter displayed in Fig. 6 is the average value of dimensionless parameter t (see Eq. (1)). It is known from theo-

retical considerations that the value of t can be correlated with the dimensionality of the conductive phase within the composite. For example, if the conductive phase forms two-dimensional structures, t will have a value of 1.3 while for ideal (isotropic) 3D structures the value of t will be 1.94 [13,14]. As can be seen from Fig. 6, the average dimensionality for the larger particles is closer to the value typical for 3D structures while the 70 nm have a dimensionality value that is between both limiting values. This again confirms the somewhat different behaviour of the smallest particles.

4. Conclusion

Continuous, nanometre-thick, carbon coating around sub-micrometer particles can only be formed if carbon content is at least about 1.5–2.0 wt.% (which in the case of TiO₂ corresponds to ca. 3–4 vol.% of carbon). When such a continuous coating is formed, the composite conductivity reaches a value of about 10^{-3} S cm⁻¹, which is probably sufficient for preparing good-performance battery electrodes. Adding more carbon can further increase the conductivity of the composite up to ca. 0.5 S cm⁻¹. The average conductivity of the carbon phase itself is estimated to about 30 S cm⁻¹. To reach this conductivity, the precursor (citrate) must be heated to at least 700 °C.

Acknowledgements

Financial support from The Ministry of Higher Education, Science and Technology of the Republic of Slovenia is gratefully acknowledged.

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