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Carbon nanocoatings on active materials for Li-ion batteries

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Abstract

Carbon coatings were prepared on various submicrometre-sized particles that can be used as active materials in lithium rechargeable batteries. As a precursor citrate anion was used which, after carbonization at 500–600 °C, transforms into a uniform, several-nanometre-thick film that is tightly adhered to the surface of substrate particles. The coatings on $Li_4Ti_5O_{12}$ and TiO_2 increased significantly the average electron conductivity of cathode composite material, which resulted in a more than 100% increase of reversible capacity at a C/3 rate. Additionally, the coating on TiO_2 prevented the gradual deterioration of reversible capacity of this material observed in absence of coating. In cases where due to temperature or atmosphere sensitivity of the substrate, carbon nanocoatings cannot be prepared, we propose the use of conductive polymers. A successful wiring using a sulphonated polyaniline is demonstrated on the example of MoS_2 nanotubes.

Keywords: Carbon coating; Conductive polymer; Lithium ion batteries; Electrical conductivity; Electrochemical wiring

1. Introduction

It is well known that the kinetics of insertion battery electrodes can be greatly improved by decreasing the active particle size. Less known, but equally important, are some recent findings[1–3] showing that in certain cases (CoO, CuO...), also the battery capacity (a thermodynamic property!) can be improved if the active material is used in nanoparticulate form instead in the usual form of micro-sized grains. The reason that, in practice, nanoparticle-based electrodes rarely show the expected kinetic supremacy is in the so-called problem of "electrochemical wiring":[4,5] it is difficult to make a parallel connection of an ionic and electron conductor from a current collector and ionic reservoir, respectively, to each individual nanoparticle. One possible solution is to coat each particle with a thin carbon coating containing enough defects (pores, cracks) to allow easy penetration of ions and, at the same time, being compact enough to take care for efficient electron wiring.[5–10]

The selection of a coating as a "wiring architecture" may have additional advantages. For example, it can serve as a mechanical and/or (electro-)chemical protection shell for the underlying active material. Until now, mostly inorganic protective coatings have been reported[11–15] while no clear data about the possible protective effect of carbon coatings on commonly used cathode active materials have been reported.

In the present work, we show that nanometer-thin carbon coatings prepared from a citrate precursor possess a kind of double functionality mentioned above. As regards their ability to electrochemically wire poorly conducting cathode materials, the previous quite convincing results on olivines[5,16] are now extended to titanium-based materials, in particular $Li_4Ti_5O_{12}$. Their protective nature, however, is demonstrated on TiO_2 nanoparticles. The latter are also used as a model material for estimation of some basic conduction properties of carbon-coated ceramic materials.

The most serious practical limitation to application of carbon coatings are the relatively high temperatures (at least 500–600 °C) needed for their formation from organic precursors. Additional limitations may arise if the active material is sensitive to the reductive environment created during the process of carbonization. It is shown that in such cases the electrochemical wiring of nanosized active materials may be achieved by the use of an electron-conducting polymer appropriately distributed among the active powder so that the access of liquid electrolyte to the active particles is not hindered.

2. Experimental

Carbon coating on $LiFePO_4$/C composites were prepared by a sol–gel method with consequent firing of xerogel in inert

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atmosphere. The preparation procedure is explained in more detail elsewhere.[16] Commercial TiO_2 anatase type particles (Riedel-Haen, 14027) with particle size between 200–300 nm and surface area 9.2 m^2/g, were used as a model substrate for preparation of carbon coating. Typically, a constant mass of TiO_2 particles with different amount of citric acid (Aldrich C8,315-5) was added into ethanol and mixed for 30 min. The slurry was dried at 60 °C. The dried composites were fired in inert atmosphere at 800 °C for 10 h (heating rate was always 10 °C/min). The obtained TiO_2/C composites were mixed with a PTFE binder (Aldrich 44,504-6) in a ratio of 9:1. The amount of carbon was determined using thermogravimetric (TG) analysis in a dynamic air atmosphere using a Mettler Toledo TA/SDTA 851 thermoanalyser in the temperature range from 25 to 700 °C. The mass difference between 105 and 550 °C was taken as the mass difference due to carbon burning off.

Alternatively, carbon-coated TiO_2 anatase type particles were prepared by mixing titanium oxide-based nanotubes with citric acid and firing the composite at 800 °C for 10 h. $Li_4Ti_5O_{12}$ was obtained from TU Delft. Carbon coatings on this material were prepared according to the same procedure as described above for TiO_2 anatase particles.

Electrodes with either TiO_2 or $Li_4Ti_5O_{12}$ material were prepared by casting and pressing a mixture of 85 wt.% of this material, 7 wt.% of a teflon binder (ALDRICH 44,509/6) and 8 wt.% of carbon black (Printex XE2, Degussa) on a copper foil and drying in vacuum at 120 °C for 24 h. The active material loading was about 2.5 mg/cm^2. The electrolyte used was a 1 M solution of $LiPF_6$ in EC:DMC (1:1 ratio by volume), as received from Merck. Preparation of pellets and measurement settings for impedance measurements is described elsewhere.[17]

Single-wall n-MoS_{2-x} NTs were grown by a catalyzed transport method using C_{60} as a growth promoter in the reaction.[18,19] Pristine n-MoS_{2-x} Nts were further used in as synthesized form or in a dispersed form (reduced size of bundles). The latter were obtained with ultrasonification of pristine material in ethanol. Electronic wiring of either pristine or dispersed n-$MoS_{2-x}I_y$ NTs bundles was achieved by mixing these materials with 10 wt.% of sulphonated polyaniline (5 wt.% solution in *N*-methyl-1-pyrolidone). The obtained slurry was spread over a copper substrate and partially dried. Round electrodes with a diameter of 8 mm were cut and pressed. The active mass (mass of n-MoS_{2-x} NTs bundles) was typically 1 mg. The obtained electrodes were dried in vacuum at 100 °C for at least 8 h, before they were transferred into a glove box (<1 ppm H_2O).

A laboratory-made three-electrode test cell was used to carry out the electrochemical tests. The working and the counter (lithium) electrodes were held apart with two separators (Celgard No. 2402) between which a thin strip of lithium serving as a reference electrode was positioned. The cells were assembled in an argon-filled glove box at room temperature.

Charge–discharge curves were recorded using an EG&G 283 Potentiostat/Galvanostat at room temperature. The constant current during cell cycling was set to a value corresponding roughly to C/3, and the geometric surface area of the working electrode was always 0.5 cm^2.

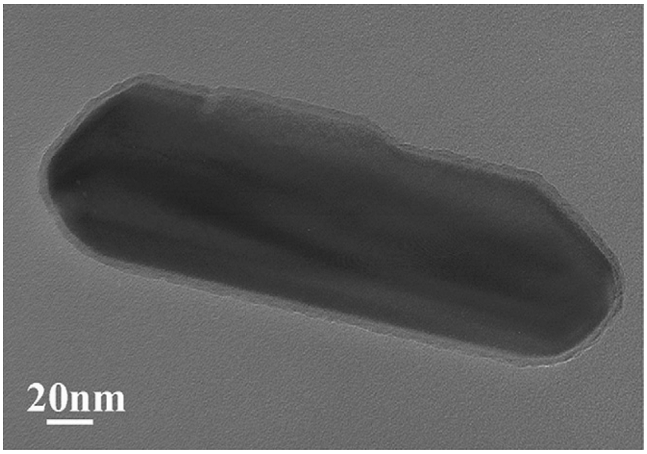

Fig. 1. HR TEM micrograph of a carbon coating on $LiFePO_4$/C particle. The whole particle's surface is covered by a carbon film of surprisingly uniform thickness. No defects (cracks, pores) are visible at this magnification.

3. Results and discussion

A typical morphology of a carbon coating obtained from a citrate-based precursor is shown in Fig. 1. Impressively, although the film is only a few nanometres thick, it covers very uniformly the whole particle's surface, that is, no cracks or a significant variation in thickness are observed. Also, it seems that there is a good attachment between the film and the particle along the whole boundary. The coating thickness can be controlled by adjusting the content of organic precursor. A detailed analysis using N_2 adsorption showed that such carbon films contain a significant amount of micropores.[16] These micropores occur spontaneously during the film formation. It is not clear whether they are essential for the electrochemical activity of the underlying substrate or not. According to one scenario, the micropores may serve as channels through which the liquid electrolyte containing lithium ions can easily penetrate thus minimizing the ionic resistance of these films. The alternative mechanism, however, assumes that in the potential window of cathode operation (3–4 V) the layered carbon structure itself is more or less "transparent" for migration of lithium ions, so no pores are actually required. Both mechanisms are consistent with the experimental observation[16] that a gradual increase in coating thickness from ca. 2 to 10 nm results in a gradual decrease of cathode performance; the thicker the coating the less permeable it is for Li^+ ions. If, on the other hand, the carbon content is decreased, the cathode again starts losing its performance. There are indications that this might be due to discontinuous carbon film. Of course, discontinuous films do not supply electrons to the whole active particle's surface – hence the decrease in cathode performance. As "film continuity" is difficult to quantify, it was necessary to find another way to determine the minimum amount of carbon in a given composite needed to effectively electronically wire the active nanoparticles. The most direct approach involves measurement of the electron conductivity of composite material as a function of carbon content. In the specific case shown in Fig. 2, the carbon coatings were prepared on commercial TiO_2 particles with an average diameter of 200–300 nm. As can be seen, a sharp

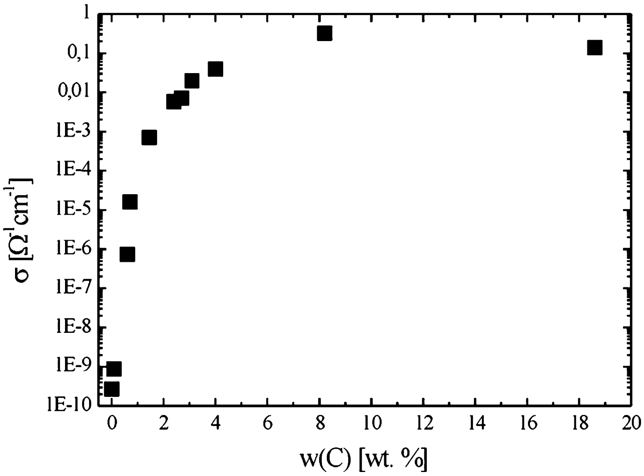

Fig. 2. Electron conductivity of TiO_2–carbon composites as a function of carbon content. The conductivity data were extracted from impedance spectroscopy measurements and geometry of the corresponding pellets prepared by pressing the composite powder at 20 MPa.

increase in conductivity occurs at about 2 wt.% of carbon while a plateau value of 10^{-1} S cm^{-1} is reached at about 5 wt.% of carbon. Interestingly, a similar carbon content range (3.2 wt.%) has been determined for the high-performance $LiFePO_4$/C cathode composites with a surface area of about 25 m^2/g. These results suggest that, when the active particle size is of the order of 100 nm, the minimum carbon content yielding a continuous coating is about 2–3 wt.%.

Based on the results in Fig. 2, we prepared carbon coatings on a $Li_4Ti_5O_{12}$ active material with an average particle size between 50 and 100 nm. The carbon content was 4 wt.%. Comparison with non-coated material (Fig. 3) shows a huge increase in capacity when cycling between 3 and 1 V versus Li/Li$^+$. A closer analysis of charge–discharge curves reveals that the increase of the capacity is mainly due to a decrease in polarization, which confirms the role of coating as a wiring medium.

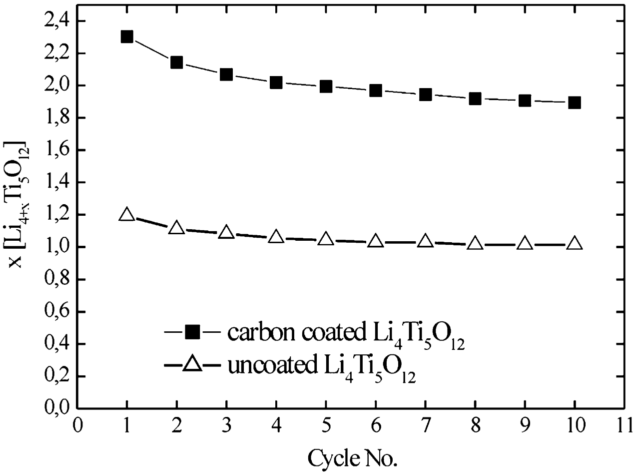

Fig. 3. Comparison of cycling behaviour of carbon-coated and uncoated $Li_4Ti_5O_{12}$ active material. The material was cycled between 3 and 1 V vs. Li/Li$^+$ at a C/3 rate.

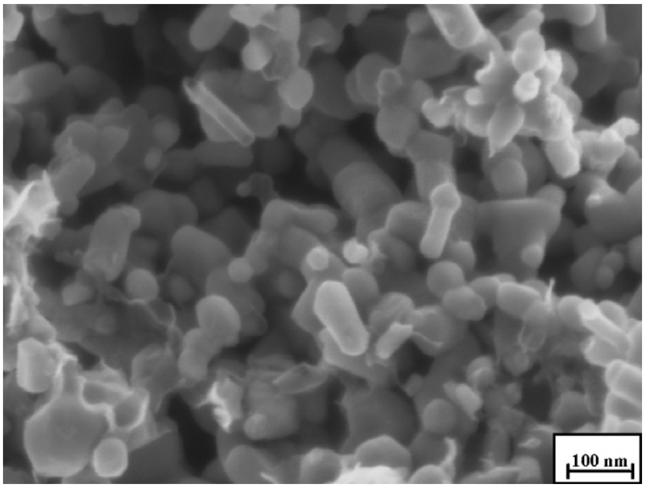

Fig. 4. Coated anatase particles obtained by heating of nanotubes in the presence of citrate. Average particle size is in the range 50–100 nm. Carbon content: ca. 5 wt.%.

The possible protective function of carbon coatings was tested on a TiO_2 material obtained by heating titanium oxide-based nanotubes 800 °C in the presence of a citrate precursor. We used nanotubes instead of particles because the former are much easier to disperse which, after heating, results in a more uniform coating. The obtained coated anatase particles are displayed in Fig. 4. The carbon content in this material was found to be about 3 wt.%. As the particles are in average somewhat smaller than 100 nm, we assume, based on the findings above, that the carbon coating is partly discontinuous or, alternatively, that some particles are not coated. Still, comparison with the entirely uncoated material (Fig. 5) shows a remarkably improved stability during electrochemical cycling. At a first sight it might seem surprising that in the first cycle the capacities of the coated and uncoated materials are equal. Namely, due to the wiring function of coating one would expect a difference similar to that shown in Fig. 2 already in the first cycle. A closer examination of the inset in Fig. 5, however, shows significant differences in the first-cycle

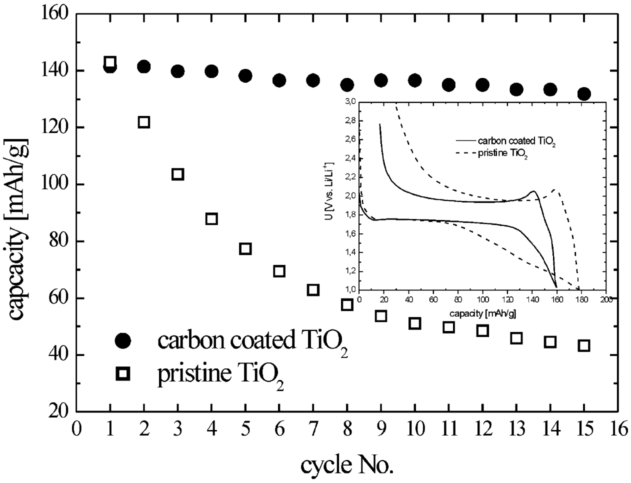

Fig. 5. Comparison of cycling behaviour of carbon-coated and uncoated TiO_2 particles. The wiring role of carbon coating is observable after ca. 10th cycle. Before that, an additional reversible capacity to that typical of TiO_2 was detected. This contribution occurs at potentials below the plateau of 1.6–1.7 V (see inset) and gradually decreases with cycling.

charge/discharge curves for both materials. Specifically, a large portion of the capacity of the uncoated material originates from processes having a potential below 1.6–1.7 V, which is typical for Li insertion into anatase. The nature of these processes is not known but, obviously, they are related to the bare surface of TiO_2 in contact with electrolyte. It is interesting that, in the first cycles, these surface reactions are quite reversible and that their capacity deteriorates relatively slowly. Once these surface processes fade out (after ca 10 cycles), the wiring function of the coating is clearly observable from the difference in capacity of coated (ca. 140 mAh/g) and uncoated (ca. 50 mAh/g) material. As a whole, the results of Fig. 5 show that besides serving as an efficient wiring medium, the carbon coating may also function as a “surface protector” inhibiting certain (unwanted) side reactions on the surface of active material.

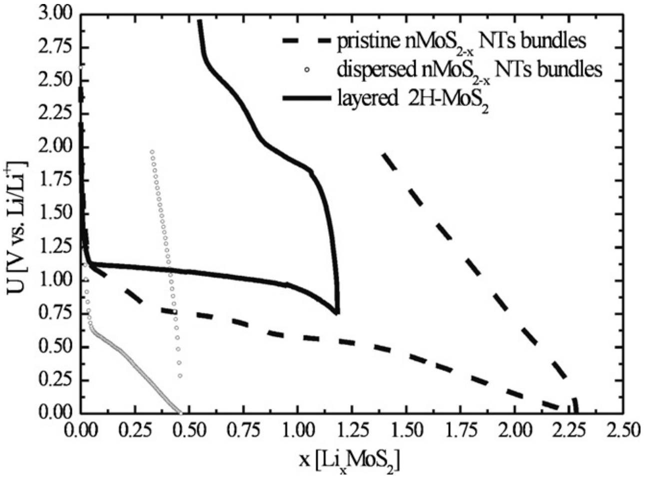

Fig. 6. Comparison of first charge/discharge curve of: layered MoS_2 (solid line) non-dispersed-pristine n-MoS_{2-x} nanotubes (dashed line) and dispersed n-MoS_{2-x} nanotubes (doted line).

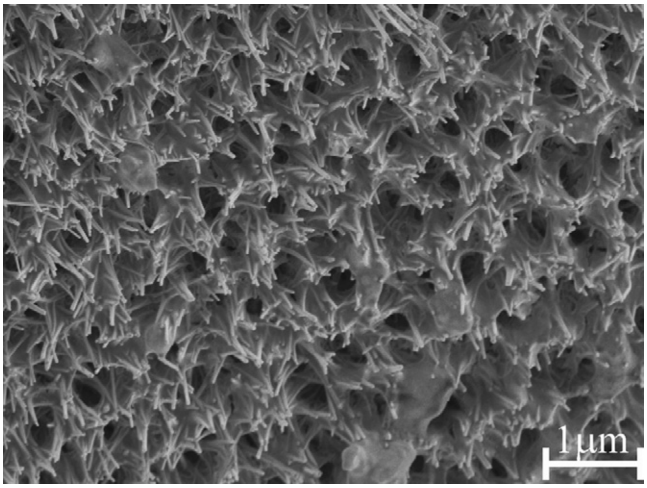

Fig. 7. Distribution of sulphonated polyaniline (seen as bulky patches) among n-MoS_{2-x} nanotubes bundles.

The in situ carbonization route is the only well-elaborated method for preparation of carbon nanocoatings possessing the electrochemical-wiring and, eventually, protective properties discussed above. Unfortunately, this method is only appropriate for substrates that are stable up to 500–600 °C and, also, that are not sensitive to reductive atmosphere. For substrate materials that do not meet these requirements, alternative-wiring strategies must be developed. One possibility, which has already given promising results,[18,19] is the use of electron-conductive polymers, such as doped polyanilines. The basic idea is simply to mix the nanoparticulate active material with an electron-conductive polymer so that all nanoparticles are attached to the polymer molecules while the latter should be interconnected in the whole volume of the resulting composite material. Beyond that, there is an additional crucial feature that such a composite must exhibit: an interconnected system of pores leading to the active particles’ surface to provide the ionic conductivity when the composite is soaked with liquid electrolyte. From the technological point of view, it is difficult to find mixing conditions that yield two parallel running and internally connected webs of polymer molecules and pores, respectively, each contacting all active particles. Various testing in our laboratory have shown that such an architecture is easier to achieve with nanowires or nanotubes than with nanoparticles. An example of the former are n-MoS_{2-x} nanotubes mixed with sulphonated polyaniline. It is expected that nanosized material will exhibit faster kinetics (leading to lower polarization and, finally, higher capacity) than its microsized counterpart. However, as seen in Fig. 6, the supremacy of n-MoS_{2-x} nanotubes over the conventional (layered) MoS_2 structure becomes only evident if the former is appropriately dispersed (compare dashed and solid line in Fig. 6). Surprisingly, the less dispersed nanotubes gave much better results. We explain this effect by referring to Fig. 7, which shows the distribution of polyaniline between non-dispersed NT bundles. It can be seen that despite thorough mixing the distribution of polyaniline is far from uniform. This means that, mostly likely, many bundles are not appropriately electronically contacted with the current collector. Still, at moderate current densities, the wiring as a whole seems to be satisfactory. If, however, the bundles are additionally dispersed, the portion of poorly contacted bundles increases, resulting in a larger overall resistance and poorer electrochemical performance (doted line in Fig. 6). To further optimize this technology, it is necessary to find a correlation between various mixing parameters (content of polymer, mixing rate, time, temperature etc.) to further improve the distribution of polymer between nanosized active entities (either tubes, wires or particles).

4. Conclusions

By carbonization of a citrate precursor it is possible to prepare carbon coatings that are uniform in thickness and adhere tightly to the substrate. The primary role of such coatings is to wire electronically the poorly conducting underlying substrate. At the same time, the coating must be permeable for lithium ions in the perpendicular direction. To meet both requirements it seems that the coating thickness must be between 1–2 nm. This means that, if the typical size of the substrate particles is in the order of 100 nm, the final carbon content must be in the range of 3–5 wt.%. The second possible function of carbon coatings is to protect the surface of underlying substrate from unwanted interactions with the electrolyte solution. An example of such a protection was demonstrated in the case of TiO_2 anatase particles prepared by thermal degradation of TiO_2 nanotubes in the presence of citrate. For substrate particles that are sensitive to high temperature or reductive atmosphere we propose the use of conductive polymers as an electron-wiring medium. A quite successful wiring using a sulphonated polyaniline has been demonstrated on the example of MoS_2 nanotubes.

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