

# ADVANCED GRAPHITES FOR LITHIUM-ION CELLS

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## Abstract

In lithium-ion and lithium polymer cells, graphites are preferentially applied as anode materials due to their high reversible intercalation capacity and cycle lifetime. The favored graphitic structure of the anode materials is typically created by a high temperature treatment. In order to cut down the necessary effort of generating very high temperatures, doping of graphite precursor materials with graphitization catalysts may be used. Additionally, this approach is a promising method to improve the graphite properties, preferably the specific capacity and the cycle life time. Studies have been carried out by doping of the graphite precursors with both metallic and non-metallic elements. As an example, the results of iron and boron doping of a pitch coke for the preparation of graphites is reported.

## Introduction

Carbon materials, especially graphite powders, are widely used as main components of anodes in lithium-ion and lithium-polymer cells. As both capacity and cycle lifetime of these cells are limited, several approaches have been attempted to substitute anode graphites by other components. Nevertheless, carbon materials are still dominating the market for anode components. In order to guarantee favorable intercalation properties, preferably a high reversible capacity, a high efficiency, and a high cycle life time, the graphite precursor materials have to be heated to temperatures well above 2500°C, typically to temperatures in the region of 3000°C. Even for ‘soft’ carbons which are characterized to be easily transformed into graphite by thermal treatment, these high temperatures are required. Throughout this thermal treatment, a rearrangement of carbon atoms takes place, defects in the structure are removed and a relaxation of distortions occurs – resulting in a synthetic graphite exhibiting a polycrystalline structure.

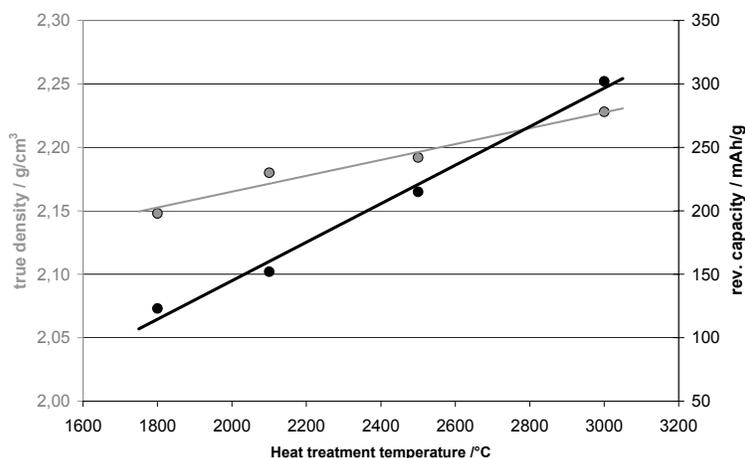
As the graphitization of carbon materials is a thermally activated process, extensive studies have been carried out in order to reduce the temperature necessary for this disorder-order transformation. It is very well known that the structure of the starting material has a strong impact on the graphitizability. ‘Hard’ carbons, produced by carbonization of highly crosslinked polymers like phenolic resins, do not exhibit a reasonable ability to form graphitic structures by thermal treatment [1]. Nevertheless, even these disordered carbon materials can be graphitized using special additives [2]. Besides the structure, the addition of special minerals or metals may influence the graphitizability of the precursor material as well as the graphitization process itself. As far back as the 19th century, E.G. Acheson discovered the catalytic effect of silicon on the graphitization of coal [3]. In the meantime, a multitude of substances have been found to be influencing the graphitization process. Typically, carbide forming elements act as graphitization catalysts by selectively attacking and eliminating reactive (non-graphitic) sites (by repetitive formation and decomposition of carbides resulting in a deposition of graphite), by dissolving disordered carbon in a liquid phase and subsequent precipitation of graphite or by increasing the carbon diffusion rate [2,4,5]. The proposed graphitization catalysts extend from the well known elements boron, silicon, iron, calcium, titanium and vanadium to magnesium, aluminum, cobalt, and nickel.

## Experiment

Coal tar pitch coke was used as starting material for the preparation of the different graphites. The addition of the doping compounds was realized by granulating the coke with an aqueous solution of boric acid (concentration in compound: 1% by weight) or iron (II) acetate (concentration in compound: 4% by weight), respectively. Subsequent to a first heat treatment step to 1000°C, the samples were thermally treated to different temperatures between 1800°C and 3000°C under Argon atmosphere. The electrochemical measurements were carried out in coin cells (counter electrode: Lithium), using 1M LiPF<sub>6</sub> (in EC/DEC 1:1) as electrolyte.

## Results and Discussion

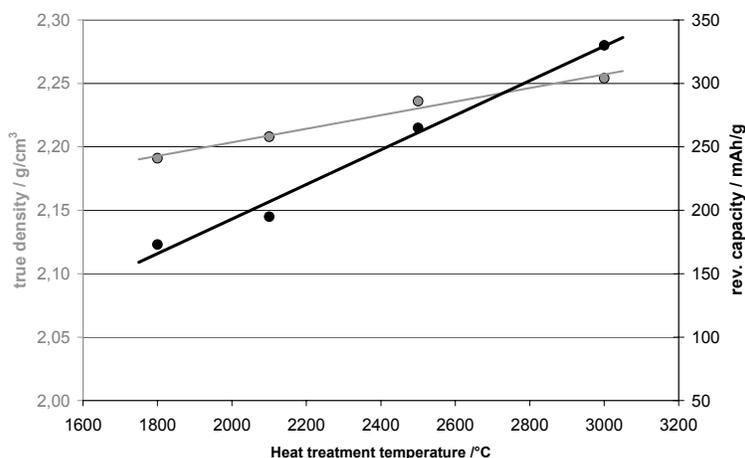
Figure 1 shows the true density (as a useful indicator for the level of graphitization) and the reversible capacity of the graphites derived from non-doped coal tar pitch coke as a function of the final heat treatment temperature. As expected, the true density of the resulting graphite rises with increasing temperature up to a final value of 2.23 g/cm<sup>3</sup>, which is close to the density of the graphite crystal (2.26 g/cm<sup>3</sup>).



**Figure 1.** True density and reversible capacity (half cell vs. Lithium) of non-doped graphites.

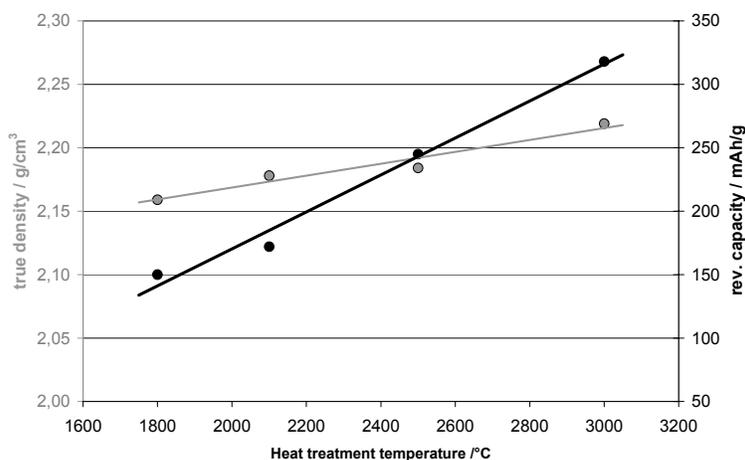
The reversible capacity shows a similar trend. Starting at a comparatively low level of about 125 mAh/g, the capacity rises to a final value of approximately 300 mAh/g, significantly lower than the theoretical (charge) capacity of graphite of 372 mAh/g (calculated for  $\text{LiC}_6$ ).

For the iron doped samples, the corresponding data are given in figure 2. Here, the resulting true density is slightly higher compared to the non-doped samples, and comparable densities can be achieved at lower temperatures, indicating the graphitization catalyzing effect of iron. The same applies to the reversible capacity of the samples. Starting at a significantly higher level of well above 150 mAh/g, the capacity rises up to almost 330 mAh/g. This corresponds to an improvement of 10% compared to the non-doped graphite.



**Figure 2.** True density and reversible capacity (half cell vs. Lithium) of the iron doped graphites.

An addition of boric acid exhibits a different performance. Figure 3 shows the comparable results for the graphites doped with boric acid. In this case, the true density starts at reasonably low values of 2.16 g/cm<sup>3</sup> and increases to almost 2.22 g/cm<sup>3</sup>, demonstrating a lower catalytic influence of boron for graphitization compared to iron. The level of the achieved densities is comparable to the non-doped samples. Nevertheless, the reversible capacity increases to maximum values of almost 320 mAh/g, significantly above the reversible capacities of the non-doped graphites. Although the final density of the graphite is still limited, boron seems to facilitate the graphitization of carbon materials via the formation of boron carbide [6]. Additionally, the remaining boron increases the intercalation capacity of the final graphites, resulting in reversible capacities comparable to graphites produced using iron salts as graphitization catalyst.



**Figure 3.** True density and reversible capacity (half cell vs. Lithium) of the boron doped graphites.

## Summary and Conclusions

As an example for catalytic graphitization, the effects of iron and boron doping of a pitch coke on the true density and intercalation capacity of the graphitized coke are reported. It can be concluded that the addition of iron as well as of boron (here in the form of boric acid) increases the intercalation capacity of the resulting graphites. Nevertheless, the addition of boric acid exhibits a less significant influence on the true density of the final graphites than expected – whereas an iron doping considerably increases the true density which has been used as an informative indicator for the level of graphitization.

## Acknowledgments

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