



Short communication

High capacity graphite–silicon composite anode material for lithium-ion batteries

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ABSTRACT

A novel silicon/graphite material prepared by a new process, in which a gelatinous silicon precursor is deposited on porous natural graphite, is introduced. The obtained composite material provides an excellent cycling stability, high coulombic efficiencies and a good rate capability. Morphology and structure of the new material were examined by SEM/TEM measurements using focused ion beam technique for sample preparation.

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1. Introduction

Nowadays lithium-ion batteries represent the system of choice for energy intense mobile application such as smart phones, laptops and other consumer electronic devices. Presently graphite or other carbonaceous materials are the most common active masses for negative electrodes in lithium-ion batteries. The theoretical capacity of the LiC_6 compound (372 mAh g^{-1}) is quite poor compared to those that are accessible with binary lithium intermetallic phases, like $\text{Li}_{22}\text{Si}_5$, with a theoretical capacity of 4200 mAh g^{-1} [1]. Unfortunately the high capacity of the Si/Li-intermetallic phases is accompanied with high volume changes during lithium insertion and extraction, whereas the difference in volume of the unlithiated silicon and the fully lithiated $\text{Li}_{22}\text{Si}_5$ phase is about 300%. As a result of the highly ionic character of the formed zintl phases they are very brittle, so that mechanical stress resulting from the high volume changes causes a rapid decay of the dimensional stability of the host material. As a consequence of the cracking and disintegration of the active material particles associated with the loss of contact to the ionic and electric conducting electrode environment those electrodes suffer from a large capacity fading [2].

Numerous efforts have been made to overcome the problems of the dimensional instability of these materials. The use of small sized particles [3–5] and nanomaterials, e.g. nanowires [6,7], the embedding of the host material into a dimensional stable matrix [8] or the use of carboxymethylcellulose (CMC) as binder [9,10] are some of these approaches.

Various methods have been investigated [11–13] for the preparation of silicon. Silicon is either accessible through electrochemical [14] or chemical reduction [15] of chlorosilanes or through thermal decompositions of hydrido-substituted [16] open chain and cyclic silanes, whereas monosilane (SiH_4) is the most common precursor by economical reasons and its good availability. Nevertheless, using monosilane (SiH_4) as precursor for thermal deposition, has some major disadvantages, due to the fact that SiH_4 is a gas at room temperature. It is not only difficult to handle (self igniting in contact with even very low concentrations of oxygen), it is also very difficult to design a process to achieve active material capable silicon particles.

It is well known that also higher hydridosilanes with the general structure $\text{Si}_n\text{H}_{2n+2}$ or cyclic ones $-\text{[SiH}_2\text{]}_n-$ are able to form silicon via thermal decomposition. However, the decomposition temperature, also of the higher silanes, is often 80–100 °C above their boiling point [17] so that they also have to be decomposed from the gaseous phase, which complicates the preparation of thin structured films or coated materials.

Cyclopentasilane (CPS, Si_5H_{10}) is known to undergo an UV-light induced polymerisation [18] under formation of polymers of vari-

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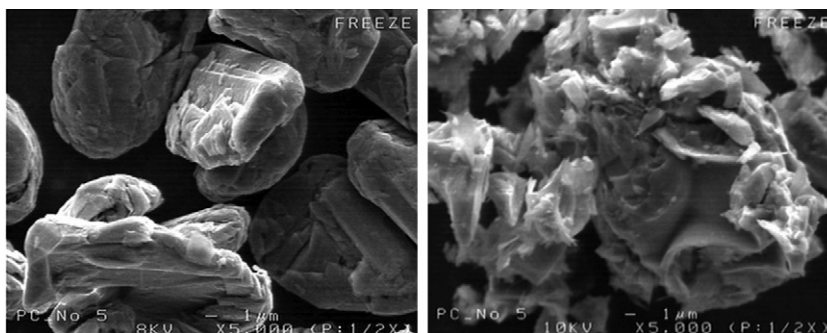


Fig. 1. SEM image of natural graphite (left, magnification 5000 \times) and of the graphite/silicon composite material (right, magnification 5000 \times).

ous chain length with molecular weights up to 2600 g mol⁻¹. These polymers have a gelatinous consistence and are able to form amorphous silicon through thermal decomposition.

In this work we investigated a new way to produce a graphite/silicon composite material as anode material for high capacity lithium ion batteries using a gelatinous silicon compound, formed from CPS, as precursor [19]. The novel design of this active material provides an excellent cycling stability, rate capability and coulometric efficiency.

2. Experimental

The CPS precursor was synthesized using the method which was introduced by Hengge et al. [20,21] in 1973. For the preparation of the electrode material the CPS precursor was exposed to 405 nm UV-light to induce photo polymerisation. During the irradiation with ultraviolet light the colourless CPS became cloudy and the colour turned into light yellow. Accompanied by this reaction, the evolution of gas was observed, which was supposed to be hydrogen. After an exposure time of seven minutes the liquid had turned into a gelatinous compound. This gel was mixed with the porous natural graphite for further processing steps. The following decomposition of the paste containing the graphite and the oligomeric- and polymeric-hydridosilanes in a mass ratio of 1:1 was done at 823 K for 2 h with a heating ramp of 15 K s⁻¹. All previous process steps were done under an argon atmosphere. After the decomposition the compound consisted of one third of amorphous silicon and two third of graphite (stoichiometry C_{2/3}Si_{1/3}), whereas the silicon was deposited on the surface and in the pores of the graphite. The gained material had to be milled by a mortar for electrode preparation.

To determine the morphology of the particles, SEM (JWS-7515, JEOL Ltd.) pictures were taken. To get information on the inner structure of the particles, they were cut with the focused ion beam technique (FIB) and afterwards transmission electron microscopy (TEM, FEI Tecnai F20 TEM/STEM) measurements were done. With HRTEM measurements the crystal dimension of the deposited silicon and the natural graphite were determined.

The prepared electrodes for the electrochemical tests were composed of 84 wt% graphite/silicon particles (20–30 μ m), 8 wt% super P as conducting agent and 8 wt% CMC as binder. The electrode slurry was prepared via an optimized dispersing technique and coated on a copper metallized non-woven 3D current collector (POLYMET[®] XII-1 Cu), predried at 333 K (air) and finally dried at 398 K under vacuum for 24 h.

All electrochemical tests were performed in a 3 electrode Swagelok[®]-T-cell using a metallic lithium foil as counter and reference electrode. The average mass load of the electrode was about 2 mg in total. A polypropylene non-woven separator (Freudenberg FS2190) was used to isolate the composite electrode from the lithium counter-electrode. As electrolyte a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC/DEC, 3/7 v/v) with 2 wt% vinylene carbonate (VC) as additive and 1 M LiPF₆ as conducting salt was used. All test cells were assembled in a dry box under argon atmosphere.

The cyclic voltammetry experiment was performed with a potentiostat/galvanostat (Adesys-Model 1612) at 293 K and a scan rate of 10 μ V s⁻¹. The long term cycling test was performed with a Maccor Series 4000 battery tester at 293 K. After one formation cycle with a *c*-rate of 0.2C and a period of constant voltage charge at 5 mV vs. Li/Li⁺ for 2 h, where the capacity was limited to 730 mAh g⁻¹, corresponding to 60% of the theoretical capacity, the cells were cycled in the potential range of 5–1500 mV vs. Li/Li⁺ at a rate of 0.5 C and a period of constant voltage charge at 5 mV for

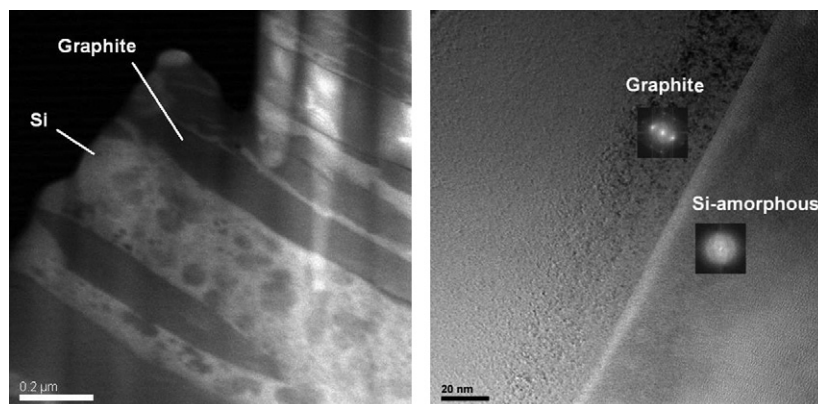


Fig. 2. TEM image (left) and HRTEM image (right) of the cut graphite/silicon particle material (right).

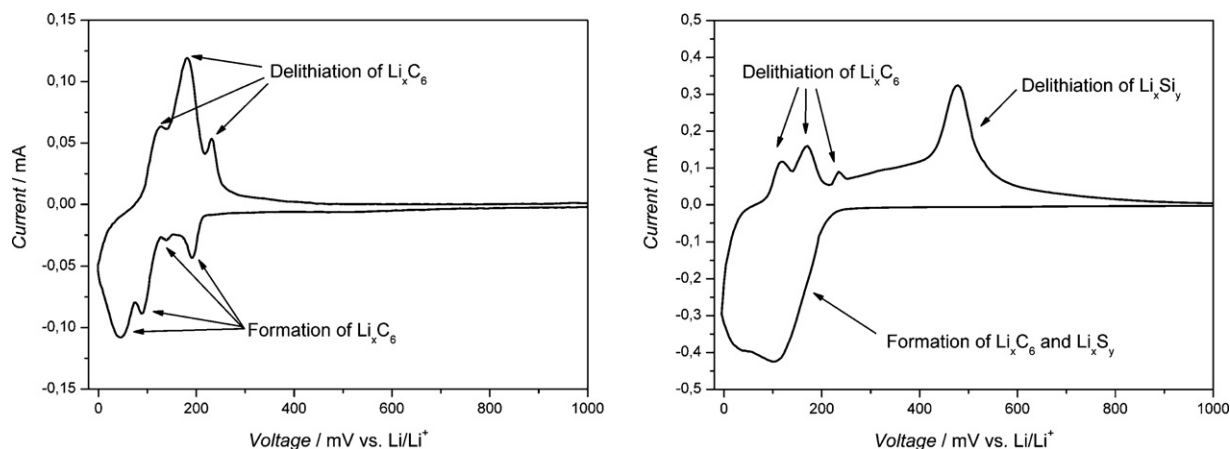


Fig. 3. Cyclic voltammogram of the first cycle of natural graphite (left) and graphite/silicon composite material (right), scan rate: $10 \mu\text{V s}^{-1}$.

2 h. The used *c*-rates were calculated with a theoretical capacity of 1200 mAh g^{-1} and from the second cycle the charge capacity was limited to 840 mAh g^{-1} . The theoretical capacity of the material was assigned by the discharge peak area of the cyclic voltammetric measurement. The current density for a *c*-rate of 1 C was 1.32 mA cm^{-2} .

3. Discussion

The SEM images clearly show a change of the shape of the particles and their surface texture (Fig. 1) due to a complete coverage of graphite with silicon. Whereas it can be supposed that the rough textured surface of the silicon is more a result of the further processing with the mortar than their native shape after the decomposition.

The active material particles were cut with the focused ion beam technique to make it possible to examine the inner structure of the particles. On the TEM images (Fig. 2, left), which were taken, it is obvious that silicon was not only deposited on the graphite surface, but also filled in the pores of the natural graphite. Due to the fact that the decomposition of the silane gel is neither accompanied with a volume expansion nor with a volume contraction, the amorphous silicon is excellent linked to the graphite without damaging its crystalline structure (Fig. 2, right). The low decomposition temperature prevents also the formation of an isolating silicon carbide interphase layer. This and the very special structure of the composite material explain the excellent cycling behaviour, although the silicon is not nano sized.

Comparing the first cycle in the cyclic voltammetry experiment (Fig. 3), a drastic change of the current–voltage curve and therefore of the electrochemical behaviour can be observed. For the insertion of lithium, the peaks of graphite and those of silicon are overlaid in the area of 250 and 0 mV. It is surprising, that even at a very low scan rate of only $10 \mu\text{V s}^{-1}$ no differentiation between the insertion reaction of silicon and graphite can be made. For the oxidation of the material (extraction of lithium) the reactions of graphite and silicon differentiate very well. For graphite we observe the expected 3 oxidation peaks, whereas the silicon shows only one at 500 mV, which is in contrast to other characterised silicon materials and also to the results reported in literature [22].

In the cycling study (Fig. 4) the capacity was limited to 840 mAh g^{-1} what complies with 70% of the theoretical capacity of 1200 mAh g^{-1} . The lower capacity in the first cycle is a result of the special formation program, in which the capacity is limited to 60% of the theoretical capacity to counter the large volume changes which occur when silicon would be fully loaded. The lower efficiency in the first cycles is the result of the film formation. After the formation a stable cycling of over 100 cycles

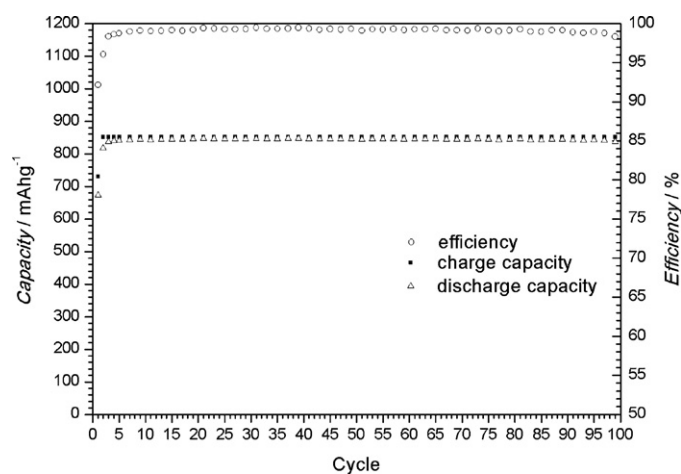


Fig. 4. Cycling study of the graphite silicon composite material (capacity limited to $0.7C$).

with an excellent efficiency of more than 99% can be observed (Fig. 4).

4. Conclusion

A new way to prepare a high capacity silicon/graphite composite material through decomposition of a gelatinous silane precursor was shown for the first time. The obtained composite material provides good electrochemical properties and excellent efficiencies, which can be explained by the novel structure of the material. In TEM measurements of particles, which used focused ion beam technique for sample preparation, a layer structure was obvious. The good embedding of the silicon in the graphite matrix make a stable cycling over 100 cycles at 840 mAh g^{-1} with an excellent efficiency of over 99% possible.

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