

A new type of nano-sized silicon/carbon composite electrode for reversible lithium insertion

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Received (in Cambridge, UK) 11th November 2004, Accepted 24th December 2004

First published as an Advance Article on the web 26th January 2005

DOI: 10.1039/b417492e

A new type of nano-sized silicon/carbon composite was developed. It shows superior electrochemical cycling properties as negative electrode material for possible use in lithium-ion batteries with respect to high reversible and low irreversible capacity, and low fading.

Lithium-ion batteries are among the most useful devices for electrochemical energy storage, because of their high energy density (more than 150 Wh kg⁻¹) and very high efficiency (up to 95% overall), which lets their use for electric vehicles (EVs) and hybrid-electric vehicles (HEVs) an option for the future.

The material mostly used for the negative electrode is graphitic carbon, because of its relative safety upon cycling when compared to lithium metal. A disadvantage of graphite is, however, the relatively low electrochemical charge capacity (theoretical value: 372 mAh g⁻¹). For many years, therefore, research has been conducted to find alternative negative electrode materials, above all in the field of lithium-metal alloys. In these systems, the metal reversibly forms alloys with lithium, which have very high capacities. A general disadvantage of alloy electrodes, however, is the huge volume change which occurs upon the insertion/deinsertion of the lithium. It can attain values of more than 200–300%¹ and leads to mechanical fatigue upon prolonged cycling.

Much research has been conducted on silicon, as it reversibly forms, alike tin, electrochemically active binary alloys with lithium.^{2–4} They can show a very high lithium content (theoretical maximum: Li_{4.2}Si), which corresponds to a theoretical specific capacity of approx. 4200 mAh g⁻¹. Nevertheless, also in the case of silicon the insertion of lithium is accompanied by a huge volume change (max. 323%). This leads to strong mechanical stress on the crystallites and, thus, to breaking and amorphisation of the particles and loss of the electrical contact.^{5–7} A rapid loss of the reversible capacity upon prolonged cycling (fading) is the result. A reduction of both, the particle and the crystallite size into the nm-range should have a positive influence on the cycling behaviour, as the mechanical stress during the lithiation process should be reduced. Following the concept of Dahn *et al.*,⁸ above all the use of nano-silicon/carbon composites should reveal favourable in this context. Experiments with nano-scale materials (particle size in the order of 100 nm) give capacities up to 1700 mAh g⁻¹ and reduced fading but, however, without being in agreement to common graphite electrodes with respect to cycle life and fading.^{9–11} A promising result has been obtained recently by Wang *et al.* with composite electrodes based on nano-silicon and a carbon aerogel. These electrodes show a stable capacity of 1450 mAh g⁻¹.¹² The

same group prepared also a promising high-capacity composite electrode by ball-milling, but these electrodes still suffer from a relatively high fading.¹³

In this study, we present a nano-scale silicon material prepared by reductive decomposition of a silicon precursor and the results obtained on its electrochemical cycling in graphite/silicon composite electrodes. This composite shows impressive results with respect to its very high reversible charge capacity and low irreversible capacity upon prolonged cycling and both, long cycle life and low fading.

The nano-silicon material was produced by a pyrolysis process of mono silane (SiH₄). The specific BET surface area (as determined with nitrogen gas adsorption measurements at 77 K) is about 12 m² g⁻¹. The material is obtained as highly structured aggregates with primary particles in the order of 50 nm with an amorphous layer at the surface as revealed by high resolution transmission electron microscopy (HRTEM). ESCA analysis (electron spectroscopy for chemical analysis) shows a certain oxidation of the silicon surface after storage in an ambient atmosphere. The scanning electron microscopy (SEM) image of the composite electrode, using 20 wt% of nano-silicon (Fig. 1) shows a homogeneous mixture of the silicon particles and the graphite matrix. The silicon particles form long aggregates which are well connected to the larger graphite particles.

Fig. 2 shows the cycling behaviour of the 20% Si composite electrode. Using a non-restricted cycling procedure an initial capacity of 1350 mAh g⁻¹ of active material (Si + graphite) is obtained whereas the capacity for the following discharge is ~1000 mAh g⁻¹. This shows that, even when taking into account the charge capacity of the graphite matrix itself (about 430 mAh g⁻¹ for the first intercalation), the nano-silicon

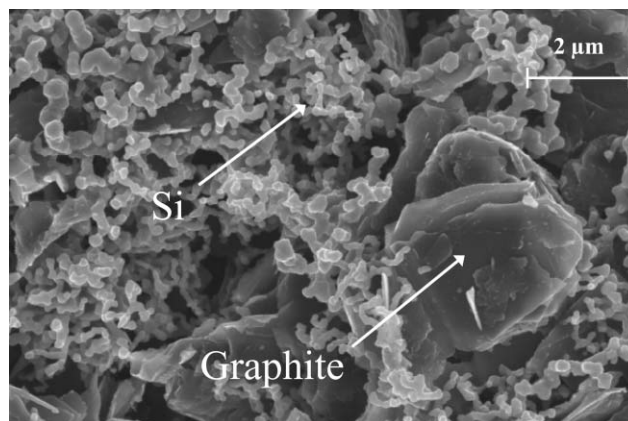


Fig. 1 SEM-image of the nano-silicon/graphite composite electrode.

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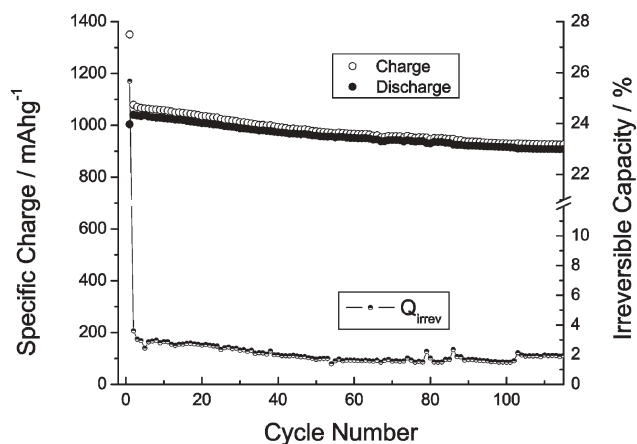


Fig. 2 Cycling behaviour of a composite electrode with 20% nano-silicon in EC : DMC (1 : 1), 1 M LiPF₆, 2% VC.

intercalates about the theoretical amount of lithium. Upon the delithiation the impressive amount of 3200 mAh g⁻¹ is liberated from the silicon part of the electrode. This shows the beneficial effect of the presence of a large amount of graphite to accommodate the volume change of the silicon. The irreversible capacity (Q_{irrev}) loss upon the first cycle is about 26%. The capacity retention upon subsequent cycling is very good with a fading of *ca.* 2% per cycle. Q_{irrev} reaches values of less than 2% after 50 cycles and the capacity fade lowers to values below 1%.

The present results are novel when compared to literature data where stable cycling with about 1000 mAh g⁻¹ are seldom reported. If so, it is for a smaller number of cycles^{13,14} or for thin film electrodes which contain a more than hundred-fold smaller amount of active material per surface unit.^{15,16} The relatively high irreversible capacity for the first cycle is, to some extent, also due to the choice of the graphite: TIMREX KS6, a small particle graphite (with high surface area to enhance the contact to the silicon particles) which shows around 24% of irreversible capacity itself.¹⁷ Our material seems, hence, to show a much smaller mechanical degradation upon the intercalation/deintercalation process when compared to traditional silicon material. This is probably due to the very small particle size and the good interaction with the supporting graphite matrix. Also the oxide-containing surface-near regions may play an important role, as the lithium oxide forming upon the first cycle from the reduction of the silicon oxide could act as a sort of binder which helps to preserve the integrity of the nano-particles upon prolonged cycling.

We also tried a second cycling procedure, consisting in the deliberate fixation of the charge capacity. It is set to 530 mAh g⁻¹ in this case (which corresponds to about 1.5 times the capacity of graphite), while keeping free the discharge capacity. The typical result of such an experiment is shown in Fig. 3. The first discharge is relatively low (with an irreversible capacity of 44%), but the following cycles rapidly show less than 2% of Q_{irrev} . The cycling can be maintained in a stable manner for more than 170 cycles. By this way the mechanical stress on the nano-silicon particles is somewhat reduced, as the reversible charge capacity calculated for the silicon part of the electrode is of the order of 1000–1100 mAh g⁻¹. In effect, as the scanning electron micrograph in Fig. 4 (obtained after 75 cycles at the capacity controlled regime)

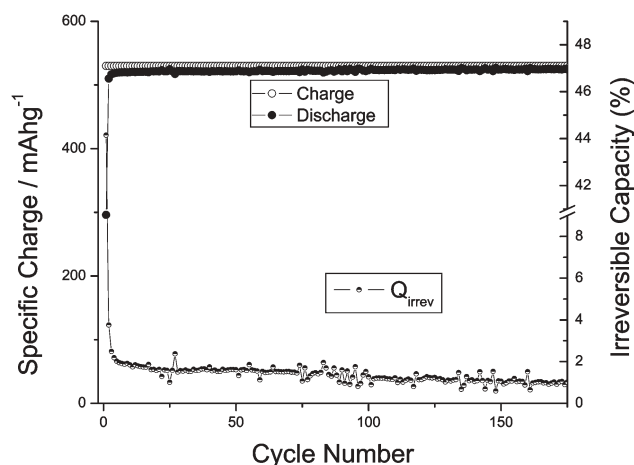


Fig. 3 Cycling behaviour of a composite electrode with 20% nano-silicon in the capacity-limited mode.

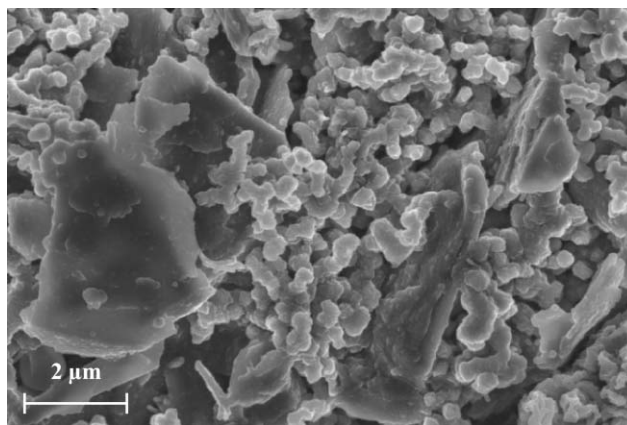


Fig. 4 SEM-image of the nano-silicon/graphite composite electrode after 75 cycles in the capacity-limited mode.

shows, the integrity of the electrode is unaltered and only the formation of a homogeneous passivation film can be acknowledged.†

TIMCAL SA (Bodio, Switzerland) is acknowledged for supplying the graphite sample.

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Notes and references

† Scanning electron microscopy (SEM) was conducted at 5 keV using in-lens detection. The electrodes were prepared as follows: the silicon material (20 wt%) is mixed with 70 wt% of a small particle size graphite (TIMREX[®] KS6, TIMCAL SA, Bodio, Switzerland) (8 wt%) and 10% of SOLEF[®] PVdF 1015 binder (Solvay SA, Belgium) in a *N*-methylpyrrolidone solution, mixed thoroughly and cast on a pre-treated (with a polymer based primer from Contitech, Nordhausen, Germany) copper foil which serves as current collector. The primer enhances the adherence of the active material on the copper. The typical mass load is 2–3 mg cm⁻². Lithium

metal is used as counter electrode. The electrolyte used is a battery grade mixture of ethylene carbonate and dimethyl carbonate (1 : 1), with 1 M LiPF₆ to which 2% of vinylene carbonate were added. The electrolyte contained less than 20 ppm of water, as determined by Karl-Fischer titration. The electrochemical measurements were conducted in combined galvanostatic-potentiostatic protocol. First, classical galvanostatic cycling with a current density of 74 mA g⁻¹ was performed until a lower voltage limit of 5 mV vs. Li/Li⁺ and an upper voltage limit of 1.0 V vs. Li/Li⁺, respectively, for the charge and discharge. At the end of each charge and discharge step a potentiostatic step followed with a reduction of the current, at the fixed upper or lower potential limit, respectively, down to a value of 5 mA g⁻¹, to complete the charge/discharge. For the first cycle, the current density was set to 10 mA g⁻¹ in the galvanostatic step in order to permit the correct formation of the passivation film on the surface of graphite and silicon. The experimental set-up used is a computer-controlled cell capture system CCCC (Astrol Electronics AG, Oberrohrdorf, Switzerland).

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