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Production of Silicon Particles for High-Capacity Anode Material, Yielding Outstanding Production Capacity

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The application of silicon as an anode material for lithium-ion batteries requires cost-effective fabrication routes and facile processing of the material. Here we present the production and characterization of silicon particles prepared using a silane-based free-space reactor, allowing control of particle size distribution and crystallinity and an outstanding production capacity. The synthesized silicon particles were chemically characterized, prepared as anode material electrodes and electrochemically characterized. The effect of active material loading and electrolyte additives was studied.

Introduction

Silicon is proven to have great potential as an anode material in lithium-ion batteries due to its high theoretical electrochemical capacity (3579 mAh/g)(1). The relatively low capacity of the commercial graphite electrode (370 mAh/g) limits the total specific energy of the cell (2). Thus significant efforts have been devoted to research on silicon as an improved anode material for lithium-ion batteries. However, silicon anodes deteriorate quickly during charging and discharging, due to large volume changes of the material during lithiation and delithiation. The volume change leads to pulverization or cracking of the electrode, hence the following degradation of cycling capacity and the stability of the material(3). Another challenge caused by the volume change at lithiation is the formation of the solid-electrolyte interface (SEI). The decomposition of organic electrolyte below ~1 V creates the SEI and for Si anodes it is of importance that this layer is stable and quickly formed. With extensive cycling and cracking of the electrode surface, the SEI is reformed and grows over time, creating longer diffusion paths for Li-ions. Numerous attempts have been undertaken to solve these problems(4,5), such as lithography of electrode structures(6,7), advanced nanotechnology approaches(2,8,9), incorporation of silicon in carbon nanotubes(10) and protective coatings(11). Most of these methods are too expensive or too complex for commercial use. The present study presents results from using a silane-based free-space reactor (FSR) in order to produce silicon particles on pilot-scale with a suitable nanostructure for use in lithium-ion batteries. This technique has the advantage of being a simple and low-cost method to produce Si particles in large quantities, while controlling the particle size and crystallinity of the material in a narrow distribution. The FSR technology has been studied for other applications over several decades(12). However, for production of cost effective tailored nanoparticles for lithium ion battery anodes the concept is quite new. Monosilane is introduced into the FSR and thermally decomposed in absence of any nucleation surface.
This type of homogeneous gaseous nucleation forms several nuclei which subsequently grow into spherical particles.

The synthesized Si particles were prepared as anode material, where the complex interactions with the active material were optimized. The loading of the silicon material was varied to study the processibility of the electrode slurry, while a buffer solution was used to control the bonding abilities of the binder. Mazouzi et al. (13, 14) have demonstrated that the buffering at pH 3 promotes covalent bonding (esterification) between the –OH groups of carboxymethyl cellulose (CMC), which significantly improves the electrode cycle life. A study of various electrolyte additives was performed, as literature reports the beneficial effects of applying vinylene carbonate (VC) and/or fluroethylene carbonate (FEC). Incorporation of VC results in the generation of poly(VC) on the anode surface, whilst reducing the LiF content and improving the cycling performance (15). The presence of FEC has been shown to create a less porous, protective SEI consisting of stable components (16, 17).

Experimental

Synthesis of silicon particles and characterization of their chemical structure

The synthesis route is thermal decomposition of monosilane (silane). The decomposition and particle nucleation is performed within a Free Space Reactor (FSR). As the name suggests, the concept of a FSR is that the transition from gas to solid happens absent of a nucleation surface, thus in free space. In the Ife FSR the layout consists of a tube passing through a number of heating zones, where the different zones have different temperatures (see Figure 1). As the monosilane gas passes through a heated zone, it is heated to the point of decomposition and forms elemental silicon. The decomposition temperature of monosilane is about 415 °C, however, certain metals may have catalytic effect on the reaction initiating the process at even lower temperatures.

![Figure 1. Schematic FSR process for the growth of Si particles.](image)

When monosilane decomposes, the favored products are higher order silanes, which subsequently decompose into even higher order silanes and ultimately silicon-hydrogen complexes and elemental silicon (18). Having several zones is motivated by the kinetics of silane and the intermediate species produced upon thermal decomposition. When silane decomposes, there are a number of intermediate species both gaseous, silicon hydrogen complexes and solids. The several heating zones make it possible to define different temperatures at the different stages of decomposition and growth, thus a defined
particle formation can be promoted. The particles may be distinct and dense, agglomerates of various sizes as well as porous structures. The rate of the temperature increase and the number of silane molecules present at the time of decomposition are crucial for the nature of the product. The concentration of silane and the pressure determine the number of silane to silane collisions and the temperature increased rate determines the probability of si-si bondage and thus how fast the process occurs. If the target is to produce very small particles <10 nm, this is easiest achieved at very low pressures and moderate concentrations, combined with a high temperature; such conditions will naturally limit the production rate. For the experiments presented here the product was single dense particles of an average size of about 0.5 μm.

The Scanning Electron Microscope (SEM) applied was a Hitachi S4800, with a maximum resolution of 1 nm (at 15 kV) and an optional setup for energy dispersive X-ray (EDS). The samples where attached to carbon film and a carbon layer was deposited through CVD over the particles in order to enhance the conductivity of the surface and facilitate a higher resolution. The X-Ray Diffraction (XRD) analysis was performed with a Bruker-Siemens D8 Advanced diffractometer with a Cu-Kα radiation and a capillary setup. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the level of impurities in the silicon samples.

Evaluation of cycle performance

A mixture of the active material (Si, ~ 0.5 μm, via FSR), carbon black (C65, Timcal) and binder (CMC, SigmaAldrich), in a weight ratio of 88:12:8, was dispersed in the solvent (a buffer solution of citric acid and KOH, pH 3, and water). The slurry was mixed either with a disperser (Ultra-Turrax IKA® T25) or via ball-milling (Fritsch Pulverisette 7, 300 rpm for 20 minutes). Directly after mixing, the slurry was coated on a piece of nanostructured copper foil (Schlenk) via tape-casting with a set height. The resulting electrode was dried in air at room temperature overnight and subsequently dried further in a vacuum oven at 120 °C for 3 h.

All electrochemical tests were performed in a crimped 2032 coin cell assembled in an Argon-filled glovebox (MBraun Labmaster SP). Lithium metal was used as a counter electrode, with a polymer separator (Celgard 3401) and 1 M LiPF6 in 1:1 EC/DMC electrolyte (LP30, BASF). Some cells were cycled with the use of various electrolyte additives, respectively 2 wt% vinylene carbonate (VC), 10 wt% fluoroethylene carbonate (FEC) or both additives. The cells were cycled at 25 °C between 0.05 and 1.0 V with a constant C-rate of C/10 (after initial 3 cycles at C/20) using an Arbin Battery cycler (Arbin Instruments). The electrochemical impedance spectroscopy was performed at room temperature with a Gamry 15.

Results and discussion

Silicon particles by Free-Space Reactor

The nucleation and growth of silicon particles from silane is a process of gradual removal of hydrogen, going from silane through higher order silanes, silicon-hydrogen complexes into a hydrogenated silicon lattice. The rate of hydrogen removal from the surface of the lattice, as well as the temperature of the lattice will influence the
distribution of hydrogen(18,19). It is quite possible to produce a hydrogen-depleted structure, if this is desired. The particle growth rate compared to the hydrogen removal rate ultimately controls the hydrogen content in the produced material. If the growth rate exceeds the hydrogen removal rate, hydrogen will be trapped in the lattice. The nature of the trapped hydrogen will be determined by the growth conditions. Post production heating may increase the mobility of the hydrogen and, if combined with a low hydrogen partial pressure outside the particle, the heating may lead to complete removal of the trapped hydrogen. The temperature at which this removal happens will be dependent of the nature of the structure, but for open structures or low range order structures, the temperature was earlier determined to about 610 °C(18,19). Furthermore, crystallinity, agglomeration and density of the particles may also be controlled in the process. Generally, several silicon particles grow in parallel and their associated hydrogen desorption determines the type of surface reactions and species at the different particles. If the number of particle to particle collisions is high in a part of the process where there are substantial surface reactions on the particles, the probability of particle to particle bondage, thus agglomeration, is high. In the presented data amorphous silicon with a low hydrogen content and mildly crystalline hydrogen-depleted silicon has been tested as anode material.

The SEM images in Figure 2 show the morphology and structure of the two synthesized silicon powders. The F3 silicon consists of non-oxidized, spherical Si particles with a somewhat broader particle size distribution centered around 0.5 μm. No impurities were detected by using EDS in the SEM analysis. From the XRD spectrum in Figure 3 it can be seen that the F3 particles are amorphous.

F4 silicon consists of smaller spherical particles, where X-ray diffraction shows an amorphous nature, with some crystalline peaks observed (see Figure 3). The particle size distribution of F4 is quite narrow, with an average particle size of 100 nm. Some impurities where detected with EDS mainly consisting of Al, thus the following electrochemical testing was performed with the F3 silicon. ICP-MS was applied to further confirm the purity of the F3 silicon. Some elements, like Fe, Ni, Cr and Al, were found in the ppm-range, however, no major impurities were detected.
Electrochemical characterization of the silicon particles

Figure 4 shows the cycling behavior of F3 silicon with a limited capacity range of 1200 mAh/g_{Si}. The first cycle was conducted without a capacity limitation, cycled at C/20, whereas the following cycles are limited at a charge capacity of 1200 mAh/g_{Si} (960 mAh/g for the total electrode mass) and cycled with C/5, with cut-off voltages at 50 mV and 1.0 V. The loading of the Si anode was 1.05 mg_{Si}/cm^{2}, corresponding to 3.75 mAh/cm^{2} based on the theoretical capacity. After 105 cycles the upper voltage limit of 1.0 V was reached, upon which the electrode capacity decreased. However, a specific capacity of 960 mAh/g (based on total anode mass) was achieved and cycled stable over 100 cycles, proving the excellent cycleability and capacity of the F3 silicon.
Figure 4. Limited capacity cycling of F3 with pH control. The cell is cycled to 1200 mAh/g_{Si} with cut-off voltages at 50 mv and 1.0 V. Inset: Constant C-rate cycling (C/10) comparing F3 with and without pH control (buffer solution) and VC as electrolyte additive.

The inset in Figure 4 compares variations of F3 silicon at a constant C-rate cycling (C/20 for the first three cycles, C/10 for the following cycles). It can be seen that using pH control, from adding a buffer of pH 3 with citric acid and KOH when preparing the slurry, can greatly increase the cycleability of the electrode. The initial capacity remains comparable (~3200 mAh/g_{Si}), however, without the use of pH control, the capacity drops at a much higher rate. This is in accordance with the findings of Gauthier et al.(18), where they used a buffer solution to influence the bonding between the silicon and the CMC binder. The results of using both pH control and VC as an electrolyte additive are also showed in the inset. The initial capacity is somewhat lower with 2 wt% VC (~2700 mAh/g), as is the irreversible capacity loss over the first cycles. However, the cell stabilizes after 10 cycles, and exhibits a much higher capacity retention. After 20 cycles, the cell with both pH control and VC as electrolyte additive shows the best cycle performance, together with a specific capacity of 1700 mAh/g.

The variation of loading (active material per square cm) on the cycle stability is examined in Figure 5. The same ratio between active material, carbon black and binder was mixed with various amounts of solvent, in order to achieve a variation in active material-loading. Loadings of 0.6, 1.0, 2.5 and 3.5 mg_{Si}/cm^{2} were achieved and these cells were cycled with a capacity limitation of 1200 mAh/g_{Si} as seen in Figure 4. The amount of completed cycles where the cell reached 1200 mAh/g_{Si} without reaching its cutoff voltages was compared for the different loadings. The most completed cycles were achieved with a loading of 1.0 mg_{Si}/cm^{2}, and an increase to over 2 mg_{Si}/cm^{2} resulted in a drastic reduction of completed cycles. The cells with 2.5 and 3.5 mg_{Si}/cm^{2} obtained only 16 and 11 full cycles, respectively. This drastic reduction in completed cycles can be
related to the increased thickness and the accompanying longer diffusion pathways for Li-ions, as well as the longer electrolyte pathways. The cells with a loading of 1.0 mgSi/cm² had a thickness of about 15 μm, whereas this thickness was three times (45 μm) as high for the cells with a loading of 3.5 mgSi/cm². The method of mixing might also have an influence on the cycling performance and can explain why the lowest loading did not obtain the most capacity-limited cycles. The electrodes with the three highest loadings were mixed via ball-milling, creating an optically very homogeneous and dispersed mixture. The electrode with a loading of 0.6 mgSi/cm² was mixed with an Ultra-Turrax disperser, and some agglomerates could still be observed after the final mixing step.

Figure 5. Analysis of completed cycles with limited capacity cycling (1200 mAh/gSi) for cells with various loading of active material per square cm. Inset: Completed cycles for cells with various electrolyte additives.

The inset of Figure 5 shows the number of completed cycles for cells with/without the use of electrolyte additives. Additives like VC and FEC are added to the commercial electrolyte (LP30) to further stabilize the SEI layer, which is a parameter of importance in overcoming the challenges with the silicon anode. However, the most completed cycles are obtained without using any electrolyte additives. Using 2 wt%, 10 wt% FEC or both additives, result in 76, 47 and 87 cycles, respectively. All cells had similar loading of Si per cm² (in the range 0.98-1.11 mgSi/cm²). The reason for the lower maximum cycle number with the use of electrolyte additives can be explained with the lower initial capacity, as seen in the inset in Figure 4. It has been observed with all electrolyte additives used, that the initial capacity is lower than the theoretical capacity, and also lower than obtained without electrolyte additives. Due to this, the limited capacity cycling of 1200 mAh/gSi can be too strenuous for the cells with VC and FEC, and should be cycled at a lower capacity to achieve a better cycling stability. Further examinations on the use of electrolyte additives are being performed.
Conclusions

Amorphous, microparticles of silicon were produced from a silane-based free space reactor, a method that is both cost-effective and up-scalable. The FSR can produce Si with a good size control and low hydrogen content. In the presented work two sets of Si particles were prepared in the 0.1 and 0.5 μm-range. The 0.5 μm-particles exhibited very low impurities and were electrochemically tested. More than 100 cycles at 960 mAh/g, based on the total electrode mass, were achieved for the amorphous 0.5 μm Si particles. A great improvement in cycling performance and stability was shown when using a pH buffer to influence the bonding properties of between binder and Si.

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