Continuous synthesis of highly-specific silicon nanopowder on the pilot-plant scale

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ABSTRACT

Silicon nanoparticles are synthesized in a hot-wall pilotplant reactor at two different operating conditions at pressures of 21 and 100 kPa, and corresponding temperatures of 800 and 1000°C, respectively. The variation of process parameters leads to adjustable particle size and morphology at production rates up to 1 kg/h. The resulting materials are analyzed with several techniques to investigate the relation between particle size, crystallinity, morphology, and synthesis conditions. In this work we present the formation of crystalline and amorphous silicon nanoparticles in the hotwall reactor and the results of subsequent electron microscopy, specific surface analysis (BET), X-ray diffraction analysis (XRD). Dispersions made from the materials are investigated by dynamic light scattering (DLS).

Keywords: nanoparticles, silicon, gas-phase synthesis, pilot plant, energy technology

1 INTRODUCTION

Nanostructured silicon has been identified as a promising material for a wide variety of energy-related applications like battery technology [1], photovoltaics [2], and thermoelectrics [3,4]. The high storage capacity of nanostructured silicon enables for example the development of high capacity anodes (4200 mAhg⁻¹) in Li-ion batteries. Furthermore, nanostructured silicon is believed to enable a sufficiently longevity, in spite of the significant volume expansion and contraction during lithium storage and release, which causes a rapid degradation in bulk silicon [1,5]. Also, the demand for silicon for solar-cell applications has rapidly grown since the beginning of the millennium [6]. Additionally, the development of thermoelectric generators that are based on material with unrestricted availability while maintaining a good figure of merit has led to the use of nanostructured materials based on doped silicon [7]. In sintered materials based on silicon nanoparticles, the nanostructure causes phonon scattering leading to materials with highly reduced thermal conductivity while providing good electric conductivity [8]. Therefore, siliconbased thermoelectrics can solve the problem of the limited

availability of conventional raw materials for thermoelectric generators.

Typically, all these application require highly-specific silicon nanoparticles with high purity and narrow size distribution as they can be generated from gas-phase synthesis. Usually, highly specific nanomaterials are available in minute quantities only and therefore, subsequent processing steps towards nanoparticle composites and functional materials cannot be studied. In this respect gas-phase synthesis processes have the additional advantage of scalability to industrial production needs.

In this paper we present results of the continuous production of nanostructured crystalline and amorphous silicon particles in reasonable amounts that can be utilized in energy technologies [7].

2 PILOT PLANT SET UP

A unique pilot-plant scale particle synthesis facility enabling three different synthesis routes using either a hotwall reactor (HWR), a flame reactor (FLR), and a plasma reactor (PLR) has been designed recently [9]. In these reactors the energy required for precursor decomposition is provided by either an electrical heat source, a flame, or a microwave-supported plasma. Figure 1 shows a photo of the pilot plant. The pilot plant exhibits a base area of about 60 m^2 and an overall height of 7.3 m, containing a multi level lab with a floor space of about 180 m².

The HWR and the FLR are located on the third level. In these reactors the process gases and the precursor gases are injected at the top of each reactor via complex nozzles. After the precursor decomposition and the particle formation, the particle-laden hot gases are delivered to the second level. While precursor materials in the FLR are burned by a natural gas flame under the presence of oxygen, the precursors in the hot-wall reactor decompose after convective heating to temperatures up to 1100°C. The microwavesupported plasma reactor is located on the ground level of the pilot plant. In this reactor all gases are injected at the bottom via a nozzle into the reaction zone, where the energy delivered by a microwave feeds a continuous plasma. In all synthesis reactors the overall gas flow with adjustable mixtures of inert process gases and gaseous precursors can reach values up to 200 l/min. The pumping unit is located

on the ground level, while an exhaust gas post-combustion system is located in an intermediate level above the pumps.



Fig. 1: Photograph of the three-level nanoparticle synthesis plant: Filter system in front of the image on the first level; reactors on the first and third level.



Fig. 2 (left): Reaction chamber of the hot-wall reactor (HWR), Fig. 3 (right): Double filter system, (A) filter cartridges, (B) gas outlet of HWR with two exhaust lines

Figure 2 shows the HWR in more detail, which can operate in a continuous mode, due to its double filter system (shown in Figure 3). The particles are filtered alternately by one of the filter cartridges (A) while the other cartridge can be released from collected particles and prepared for further operation. Additionally, this system enables to separate particles, which are generated in the first minutes of production process from those particles, which are synthesized later under stable operating conditions.

3 SYNTHESIS OF SILICON NANOPARTICLES

Silicon nanoparticles can be produced in the electrically-heated hot-wall reactor (HWR) at variable process conditions varying the pressure between 15 and 100 kPa and the temperature between 800 and 1100°C leading to variable particle size and morphology. Typically, particles are formed at a precursor concentration of 1 to 10 vol% monosilane (SiH₄) in a H_2/N_2 atmosphere. The resulting materials are routinely analyzed with several techniques to investigate the relation between the synthesis conditions and the resulting particle size, crystallinity, and morphology.

In this paper we present two synthesis routes for silicon nanoparticles, firstly, the generation of crystalline silcon nanoparticulate powder and secondly, for amorphous material. Both are performed in absence of oxygen. The process gases (sheath and carrier gases) and the monosilane precursor are injected at the top of the reactor. After the decomposition of monosilane and the formation of silicon particles in the hot zone, the particle-laden gases are pneumatically delivered to a filtration system (Fig. 3).

3.1 Controling the morphology and structure

For the generation of crystalline material a pressure of 100 kPa absolute and a temperature of 1000°C has been used for the synthesis. Typically, the growth of crystalline particles is observed at temperatures in this regime. At an operating pressure of 100 kPa the residence time of the particles within the reaction zone is comparatively long, which favours the formation of highly crystalline particles. For the generation of amorphous material the temperature is decreased to 800°C and the operating pressure is set to 21 kPa. Hence, the formation of the crystalline phase is reduced and the amorphous phase is favored due to reduced temperature and residence time. A precursor concentration of 3 vol% silane in a H_2/N_2 atmosphere is kept constant during the synthesis.

Electron microscopy investigations on the crystalline material revealed the formation of sintered particles with distinctive necks between adjacent particles and particle sizes around 150 nm. TEM investigations of the amorphous material showed soft agglomerated particles smaller than 40 nm. Figure 4 shows a TEM micrograph of a typical crystalline material.

X-ray diffraction analysis (XRD) is used to prove the influence of the synthesis conditions on the crystallinity. Figure 5 shows typical XRD patterns of nanoparticulate silicon synthesized at 800 and 1000°C, respectively. The analysis of the crystallite size from the full width at half maximum showed that the silicon nanoparticles produced at 1000°C and 100 kPa consist of crystallites of about 30 nm in diameter, while particles generated at 800°C and 21 kPa, exhibit a significant amount of amorphous material. The position of the Bragg reflexes of the crystalline material can be assigned to those of bulk silicon. The XRD analysis of the amorphous samples confirms the absence of crystalline material (see figure 5).



Fig 4: TEM image of crystalline silicon nanoparticles from the hot-wall reactor.



Fig 5: XRD analysis of crystalline (black) and amorphous (red) silicon nanoparticles.

3.2 Long-term performance

The production of the crystalline material was performed in a continuously running process with for 30 h, while the synthesis process of amorphous material lasted for 28 h. To demonstrate the long-term stability of the production process, both, the batch samples of the crystalline and the amorphous materials are extracted from the process at different points in time during the synthesis process and analyzed using the BET method to determine the specific surface area. The results reveal a specific surface area of ~17 m²/g for the crystalline material and ~68 m²/g for the amorphous material. These values correspond to 151 nm and 38 nm diameter for spherical particles. Figure 6 shows the specific surface area of the crystalline and amorphous silicon nano material at different times of the synthesis process. A deviation of the specific surface area smaller than 5% for the analyzed batch samples can be seen.

Therefore, the analysis reveals constant product quality of the gas-phase-synthesized materials from the pilot-plant facility. Furthermore, due to the relatively high precursor concentration compared to lab-scale systems, several kg of highly specific materials are produced during the process cycle.



Fig 6: Specific surface of crystalline and amorphous nanoparticles versus process time.

4 TRANSFER OF NANOPARTICLES INTO STABLE DISPERSIONS

Typically, industrial applications require the transfer of the functional particles into dispersions for further processing. We present three approaches for the formation of dispersions: ultrasonic bath, ultrasonic sonotrode and ball milling.

Dynamic light scattering (DLS, Beckman Coulter DelsaTM Nano C) was used to measure the size of the dispersed nanoparticles. For DLS analysis, dispersions of 2.7 wt% Si nanoparticles in acetone were produced using the three techniques. In both cases of sonication, the overall volume of the dispersion was kept constant at 60 ml for the duration of 120 minutes. The ball milling process was performed for 120 minutes using ZrO_2 balls with a diameter d_b of 500 µm and 100 µm, respectively.

Results of the DLS measurements on amorphous materials are shown in Figure 7. Figure 7a shows the normalized intensity distribution of the suspension after treatment in the ultrasonic bath, with the ultrasonic sonotrode, and the ball milling processes. The displayed data are received by averaging a minimum of four independent measurements. They reveal that the size distributions received by ball milling are smaller than those from ultrasonic treatments. Figure 7b shows the results of the D_{10} , D_{50} and D_{90} analysis for the different dispersion methods.



Fig 7: (a) DLS measurements on dispersions of amorphous silicon nanopowder in acetone produced by different dispersion methods. The maxima of the normalized graphs indicate the mean particle size. (b): D_{10} , D_{50} and D_{90} values of the suspensions displayed in (a).

While the D_{10} and D_{50} values are not significantly affected by the dispersion methods, the D_{90} value decreases for ball milling by more than a factor of two. Furthermore, sonotrode treatment, which usually couples more energy into dispersions compared to ultrasonic baths treatment leads to a significant decrease in the D_{90} value. Especially, ball milling breaks up aggregates with higher diameters and therefore the D_{90} value is reduced. The experiments reveal that the size of the milling balls $d_{\rm b}$ corresponds to the maximum diameter of the aggregates within the suspension.

Further milling experiments with balls $d_b = 100 \ \mu m$ and different process times at amorphous silicon have shown, that the *D*-values are mostly unaffected by higher milling times. The smallest *D*-values have been observed for 120 min treatments. Figure 8 shows the variation of the *D*-values in dependence on the milling time.



Fig 8: *D*-Values of amorphous silicon aggregates in acetone after 120 min with ZrO_2 balls with $d_b = 100 \ \mu m$.

5 CONCLUSIONS

Gas-phase synthesis is a highly suitable method to mass produce nanostructured materials. We have shown that highly specific silicon particles can be produced in significant amounts over several hours without losing their specifications. The materials can be post-processed using different dispersion techniques to generate suspesions, which contain highly specific materials.

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