

SINANODE[®] Materials: Key Concepts

1. SINANODE[®] active anode materials:

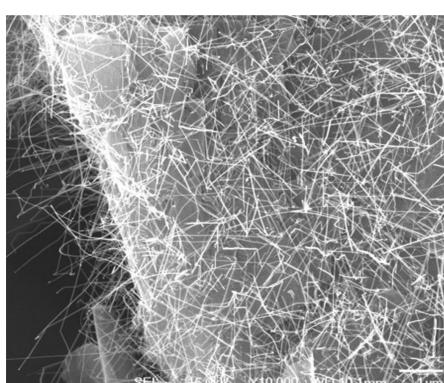
SINANODE[®] powders are active anode materials ready for use in preparing a slurry and coating electrode foil using existing industrial electrode coating equipment and processes.

The powders consist of commercial anode-grade graphite particles with silicon nanowires attached onto the surface of each particle. Typically, the silicon nanowires have a diameter between 20 and 40 nm (= 0.02 to 0.04 microns) and a length between 500 nm and 2000 nm (0.5 to 2 microns), with an aspect ratio (length/diameter) typically between 25:1 and 75:1. On a graphite particle, there may be several hundred thousand silicon nanowires attached at one end to the graphite substrate. Because of the very small diameter, the attached ends of the nanowires occupy only around 1% of a graphite particle's surface area. Because of their very small volume, one hundred billion silicon nanowires weigh less than 1 milligram.

The picture and SEM image below show the SINANODE[®] powder (left) and the silicon nanowires on a portion of a graphite particle (right):



SINANODE[®] powder



silicon nanowires on a portion of a graphite particle

2. SINANODE[®] electronic conductivity:

The attachment of each nanowire onto the graphite substrate provides a permanent electrical contact thru which electrons can flow during cycling. In a SINANODE[®] electrode, the anode layer consists of graphite particles held together and adhering to the copper current collector with a commercial binder. The silicon nanowires are exposed to the lithium-ions in the electrolyte filling the pores between graphite particles. Prior to the first cycle, the silicon nanowires are polycrystalline.

During anode lithiation, lithium ions intercalate within the graphite and also insert into the silicon nanowires, forming an amorphous lithium-silicon alloy. The electrons are supplied by the copper foil thru the network of graphite particles and conductive additive particles, and thru the attachment point of each nanowire onto the graphite. During cycling, the silicon nanowires are free to expand and contract within the pores between the graphite particles, which provide an electrically and mechanically stable anode layer. This configuration also reduces the swelling of the silicon-graphite anode layer.

Silicon nanowires provide an excellent way to achieve higher capacity at high C-rates for at least three simple reasons.

- First, the small diameter of the silicon nanowires provides a large fraction of silicon atoms near the surface and a smaller fraction within the core region of each nanowire. This ensures that the stress created by the large volume expansion resulting from inserting up to 3.75 lithium atoms per silicon atom (as in a Li₁₅Si₄ alloy) can be quickly released thru relaxation of the nanowire's surface energy.
- Second, the small diameter and high aspect ratio of the silicon nanowires allow for the rapid diffusion of the lithium ions from the surface to the core: the distance is much shorter than in the graphite particles, and the diffusivity of the lithium ions thru the already alloyed surface layers into the remaining crystalline core is excellent.
- Third, once lithiated, the silicon nanowires are amorphous and flexible and are no longer crystalline and rigid. Lithium acts as a dopant, and electron mobility is thus excellent. The nanowires efficiently conduct electrons along their length thru the graphite interface at the attachment point. This electrical path is unaffected by Si volume changes or SEI formation.

Taken together, the large surface area, fast lithium diffusion and excellent conductivity thru a reliable and permanent attachment point to the graphite, allows for high anode specific capacity even at high charge and discharge rates.

3. SINANODE[®] anode capacity, SEI and cycle life:

In hybrid active materials which combine silicon (Si) with graphite (C), the silicon can be in the form of silicon nanowires (Si NWs) or in the form of silicon nanoparticles (Si NPs).

During the cell formation cycles, an SEI (Solid Electrolyte Interface) layer must be formed on the surface of the silicon nanostructures to stabilize the high reactivity of the silicon and prevent continued decomposition of the electrolyte, which can lead to fading and shorter life due to poor capacity retention.

The anode specific capacity is increased by the amount of silicon, since Si has a much higher capacity than C. The maximum (theoretical) amount of lithium that a Silicon-Graphite composite active material can store is given by the following equation:

$$\text{Max Specific Capacity (in mAh/g)} = [X \% \cdot (3579) + (1 - X) \% \cdot (372)]$$

where "X" is the weight ratio Si/C in the composite active material; 3579 mAh/g corresponds to the alloy Li₁₅Si₄ and 372 mAh/g corresponds to LiC₆

For example, if X = 10% then the maximum specific capacity is 358 + 335 = 693 mAh/g, indicating that about half of the lithium is stored in the silicon and half in the graphite. If the number and/or length of the nanowires is increased to reach, for example, X = 20% Si/C weight ratio, then the maximum specific capacity is 716 + 298 = 1014 mAh/g, indicating that 70% of the lithium is stored in the silicon and 30% in the graphite. Unlike silicon oxide, where the oxygen atoms add weight but no capacity, the SINANODE[®] materials leverage silicon and graphite without adding inert "overhead" atoms.

After the first cycle loss (typically around 10%), the retention of reversible capacity over 600 to 1000 cycles depends in part on the SEI layer formed during the first few cycles.

It is very well known that silicon surfaces are very electrochemically active and an SEI must be formed to passivate these surfaces and reduce or eliminate the consumption of electrolyte during cycling. Thus, it is important to minimize the total surface of silicon in the composite material. It is also important to use silicon nanostructures, which are small enough to allow the silicon to cycle without fracturing.

Thus, it is useful to compare two composite materials, both with the same ratio Si/C, i.e. with the same amount of silicon per kg of active material, but with different silicon nanostructures: silicon nanowires and silicon nanoparticles.

For a given total amount of silicon (for example 100 grams of Silicon per kg of Si/C active material), one can compare the surface areas of the Si NWs and Si NPs required. The lower the silicon surface area, the better: less electrolyte will be decomposed to build an SEI layer onto the silicon nanostructures.

3.a. Equivalent volumes of silicon between nanowires & nanoparticles

Let's compare the volumes of a Si NW (i.e. cylinder of length "L") and a Si NP (i.e. sphere), both with a radius "R":

$$V_{nw} / V_{np} = (\pi \cdot R^2 \cdot L) / (4/3 \cdot \pi \cdot R^3) = 3/4 \cdot L/R = 3/4 \cdot L/(D/2) = 3/2 \cdot \alpha$$

(where alpha = L/D is the Si NW aspect ratio, which is typically > 25. For example, if the Si NW radius is 10 nm and the length is 1000 nm, then the aspect ratio L/D = 50)

Thus, if "X" kg is the weight of "N" Si NWs per kg of composite active material, then we need "M" Si NPs to get the same amount of silicon, where M = 3/2 * alpha * N. The higher the aspect ratio, the greater M: more nanoparticles are required to have the same amount of silicon as a nanowire with the same radius R and a length L = 2R * alpha. For example, if the aspect ratio is 50, then it takes 75 nanoparticles of silicon to have the same amount of silicon as in 1 silicon nanowire (assuming that both have the same radius). Note that the greater the nanowire aspect ratio, the more nanoparticles are needed to have as much silicon as in one nanowire.

It is also interesting to note that the area of a nanowire is 2 * pi * R * L and the volume is pi * R^2 * L. Thus, for nanowires, the A/V ratio is equal to 2/R, which is independent of the length L. In other words, as the length is increased (or the number of nanowires of length L is increased), the Area to Volume ratio does not change. In contrast, as the number of nanoparticles is increased to match the volume of the longer nanowires, the total area/volume ratio of these nanoparticles increases.

3.b. Comparing the total surface areas of Si NWs and Si NPs:

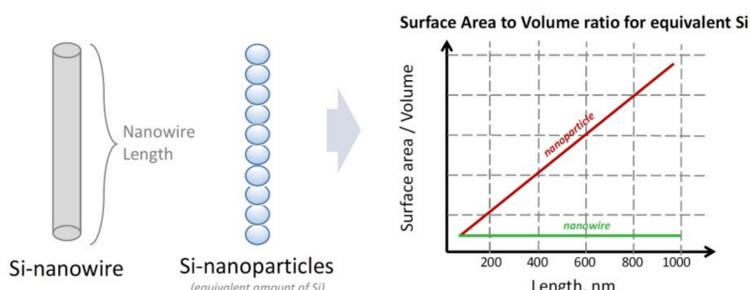
First, we compute the ration of the surface area of one Si NW to one Si NP:

$$A_{nw} / A_{np} = [2 \cdot \pi \cdot R \cdot L \cdot (1 + 1/\alpha)] / (4 \cdot \pi \cdot R^2) = 1/2 \cdot (\alpha + 1)$$

Second, we compute the area ratio for "N" Si NWs to that of "M" Si NPs (same total volume, i.e. same Si weight):

$$(N \cdot A_{nw}) / (M \cdot A_{np}) = 1/2 \cdot (\alpha + 1) \cdot N / M = 2/3 \cdot (1 + 1/\alpha) / N \approx 2/(3 \cdot N)$$

Because N is typically very large, the total surface areas of the Si NWs is much smaller than the Si NPs required for the same amount of silicon. The A/V ratio for each Si NW is still very high, enabling fast lithiation/delithiation cycles without cracks.



The diagram above illustrates the mathematical comparison of A/V between Si NWs and Si NPs.

Conclusions:

Thus, by providing silicon in the form of nanowires rather than nanoparticles, the silicon surfaces are much smaller, hence the amount of SEI to be formed is far less. In addition, the electronic path from nanowires to current collector is always maintained thru the graphite, unaffected by the large silicon volume changes, i.e. increases during lithiation & volume decreases during de-lithiation.

This helps explain the low first cycle loss, high reversible capacity and good cycling performance (i.e. reversible capacity retention) of SINANODE[®] electrochemical cells over a long cycle life, even at higher C rates.