Nano-silicon carbon hybrid particles and composites for batteries: fundamentals, properties and applications

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1. Introduction

Silicon nanoparticles have interesting properties for Li-ion batteries. Today, batteries use graphite (natural or synthetic) as negative electrode. Graphite is used as anode active material since the very beginning of Li-ion batteries and compared to the positive active materials, its evolution has remained low and is mainly centered on the interface with electrolyte for improved durability at high temperature. Graphite is particularly interesting for its good stability during electrochemical cycling, its low cost, its large availability and its relatively high capacity (350-375 mAh/g based on the LiC_6 formation versus 180-250 mAh/g for cathode active materials). Its main drawback is the quasi-absence of improvement perspectives for capacity. Other materials offer potentially much larger capacities, among them silicon and lithium appear to be the most promising with storage capacities of 3579 mAh/g (for $\text{Li}_{15}\text{Si}_4$ phase) and 3860 mAh/g¹, respectively. They both have very good capacities, large availabilities (contrarily to germanium for instance) and good techno-economical potential. However, lithium faces large technological challenges which have not been solved yet: anode volume expansion with loss of contact with the current collector, with dendrites formation and unreacted lithium are the main challenges.²

This chapter will explain why nano-silicon/carbon hybrids particles have strong interest for Li-ion applications, especially to limit SEI (Solid Electrolyte Interface) related irreversible capacities. This is made possible by the association of a rather old chemistry (carbon) with silicon particles nanotechnologies to form an active Si/C material. This material meets various well-defined requirements: mainly performances in terms of cycling stability at high capacity values (at least 600 mAh/g) along with cost effectiveness.

2. Nano-silicon for batteries

a. Silicon generalities

Silicon has a huge interest for energy storage, due to its ability to form alloys with lithium. This property has been largely studied^{3, 4} and the main alloys at room temperature are $\text{Li}_{13}\text{Si}_4$; Li_7Si_3 ; $\text{Li}_{12}\text{Si}_7$; LiSi and $\text{Li}_{22}\text{Si}_4$ as found in the Li-Si binary phase diagram. The $\text{Li}_{22}\text{Si}_5$ alloy is the richest in lithium and has a theoretical capacity of 4200 mAh/g but its formation is not observed under normal electrochemical conditions. Their electrochemical domain is illustrated below along with the corresponding volume changes and particles size increases.

In situ XRD studies indicates that the lithiation of crystalline silicon is made progressively, leading to a succession of amorphous alloys. Erreur ! Signet non défini., Erreur ! Signet non défini., 5, 6 7

By in situ NMR spectroscopy, some lithium silicon alloys have been observed along discharge and charge cycling and have been attributed to amorphous Li_2Si , $\text{Li}_{3.5}\text{Si}$ and crystalline $\text{Li}_{3.75}\text{Si}$ ($\text{Li}_{15}\text{Si}_4$)^{8, 9, 10}. At the end of discharge below 50 mV, the crystallized $\text{Li}_{15}\text{Si}_4$ phase is observed.^{11,12,13} For this alloy, the volumic expansion is 270%. Erreur ! Signet non défini., 14, 15 For spherical particles, it means a particle diameter increase of 55%.¹⁶⁻¹⁷ The following MET picture indicates that reduction is progressive from the separator side.¹⁷ After delithiation, silicon is amorphous.

Figure 1: Silicon particle size evolution and Li_xSi alloy stoichiometry during lithiation (corresponding electrochemical capacities in yellow dots) Erreur ! Signet non défini., 18, Erreur ! Signet non défini.

Figure 2: TEM image of silicon electrode after partial lithiation¹⁷

In the case of particle, lithiation occurs at the surface of the silicon particles. Uncompleted lithiation can leave a crystalline core surrounded by a lithiated surface.

b. Nanosizing

Due to the high volumetric expansion during cycling (up to 270% for the $\text{Li}_{15}\text{Si}_4$ phase), decrepitation is observed for particles larger than 150 nm.^{19,20,21} This leads to electrode cracking at large scale as shown below with a silicon wafer.^{22,17}

Figure 3: SEM picture of a silicon wafer, showing fractures after delithiation.¹⁷

During cycling, the particles bigger than 150 nm fracture progressively and this has two detrimental effects on the electrochemical cycling stability: electrical contact within the electrode materials is partially lost and the particles surface is drastically increased.^{22,, 17}

A way to avoid swelling and cracking is the use of only a small fraction of the silicon by reducing the voltage range (especially by increasing the low cut-off voltage) to limit lithiation and swelling. This has been made with micrometric particles.²³ However, in those types of formulation, the silicon capacity is reduced to 1000 mAh/g, meaning that 72% of the silicon is unused.

c. Various forms of nano-silicon

To get particles below 150 nm, the main approach is bottom-up particles preparation. Indeed, the top-down approach is usually based on particles crushing leading to large size distribution, especially with difficulties to avoid some large particles.²² Moreover such low particles size requires usually ball-milling in liquid media with solvent under inert atmosphere and high energy.

Bottom-up approach enables a much better control on the particle morphology and size distribution. The different forms are:

- Nanofilms²⁴

Despite good specific capacities, the overall anode surface capacity is limited as the electrode thickness is very low. Thickness increase leads to a sharp decrease of the electrochemical performances.²⁵

- Nanowires²⁶

Those 1D material includes nanotubes²⁷ and nanowires.²⁶ Their interest is that they can grow directly on the current collector with a limited use of conductive additives and binders. Energy densities can be high but as the length of the tubes and wires is limited, the anode overall surface capacity is usually low.^{28,29}

- Spherical particles and string of spherical particles²⁸

Laser pyrolysis is a well know technique for nano-silicon synthesis. It has been reported for the first time in 1980 by Mara.³⁰ In a way similar to most bottom-up approaches, the precursor is a gas, usually silane or chlorosilane. The silicon-hydrogen bonds are excited and broken by a CO₂ laser leading to the direct formation of silicon and dihydrogen (with silane). The use of a laser enables a very good control of the reaction zone and, therefore, of the particle size distribution.³¹ This method has been scaled up to industrial size.²⁹ Powders obtained by this process have spherical primary particles aggregated as strings of few particles. As a negative electrode the powder state enables various formulations and high loadings.⁸⁵

Figure 4: Principle of laser pyrolysis ³¹

d. General behavior and SEI

Silicon nanoparticles solve the cracking problem, but they develop high surface areas: 150 nm spherical particles have a surface area of 17 m²/g for instance and 65m²/g for 40 nm spherical particles. During complete silicon lithiation, a low potential is reached and the electrolyte salt and solvent reacts with the particles and form the well documented SEI.⁵² This usually occurs at potential below 0,8 V vs Li/Li⁺.^{32,33} An irreversible consumption of lithium and silicon occurs. This layer has a good ionic conductivity but a poor electronic conductivity.^{33, 19, 34} To form a stable layer, a “formation cycle” is usually run at a slower C-rate than the following cycles or higher temperature. During cycling, the volume expansion can leave new bare silicon surfaces. The SEI is form at the interface and causes an increase irreversible capacity upon subsequent cycling. . Many works are under way to improve the electrolyte in order to form a more stable SEI ^{35,19, 36, 37} :

Around silicon particles, the usual surface layer is made of silicon oxide (Si-O-Si) and silanol groups (Si-OH). This oxide can react with the decomposed PF₆⁻ anion to SiO_xF_y species and HF can also form SiF₆²⁻ anions. Those compounds form cracks at the Si particles surface. Interestingly, those cracks are less important for Si particles smaller than 150 nm.¹⁹

The classical solvents of the electrolyte are alkyl carbonates that can also react with the silicon and the fluorinated SEI (containing species like LiF, LiP_xF_y et LiPO_yF_z) thus increasing irreversible capacities. This phenomenon is more important with small particles and larger specific surface areas.¹⁹

The SEI containing organic and inorganic species is formed upon the first lithiation but also evolves upon subsequent cycling in the case of Si due to volumetric expansion, crackings, and exposure of fresh surfaces. This is the main drawback of silicon as negative electrode for Li-ion batteries. Two main complementary ways are investigated as workarounds:

- modifying the electrolyte formulation to make it more stable upon cycling by the use of additives such as FEC and VC.³⁸ This is not the topic of this chapter.
- protecting the silicon to reduce and stabilize the SEI formation. This chapter describes the most documented approaches which is the use of carbon.

3. Carbon

Carbons are the most used materials for Li-ion batteries. The chemical stability and specific capacity of graphite made it the most efficient material in batteries. This paved the way for the first Li-ion batteries commercialization by Sony in 1991 based on Yoshino *et al.* patent.³⁹

Table 1: Comparison of the performances of graphites and silicon⁴⁰

	Artificial graphite	Natural graphite ⁴⁰	Si
Capacity (mAh/g)	365	350	Up to 3576
First irreversible capacity	90-94%	90%	75-80% without C protection and usual formulation, up to 90% with coating
Metric Tonnage 2017	70 000	50 000	< 10 t

To combine the stability of carbon with the capacity of silicon, the mix of silicon and carbon (mainly graphite) has been tested. This way is simple but requires the development and use of specific binders which are not always easily and economically available. This is why nanoparticles of silicon hybridized with carbon have been developed.

One important feature is the thermodynamically favorable reaction of silicon with carbon to form silicon carbide which is not active for lithium storage⁴¹ and thus its formation should be avoided.:

However, the activation energy for this reaction is high and it does not occur below 900-1000°C. On the other hand, graphite is the best carbon phase for lithium storage but its formation requires hours of crystallization at temperatures above 2400°C.⁴³ Therefore, graphite/silicon composites can only be made by mixing and not by synthesis, without direct bonds between them. Some teams succeeded in forming graphene coating⁴⁴ on silicon thanks to a very special CVD parameters set : CH₄ and CO₂ at 1000°C leads to graphene growth on silicon whereas at 900°C graphene is not well formed and at 1100°C silicon oxide layer was too thick. Without CO₂, SiC is readily formed. In full cells configuration,

capacity drops by 28% after 200 cycles, with an initial capacity of 970 mAh/g. These results were achieved with 100 nm silicon powder.

However, other forms of carbon can store lithium and can be useful for silicon hybridization.

a. Carbon forms

Two properties are important for carbon as anodes materials: electrical conductivity and lithium insertion/intercalation. Both of those properties are favored with the presence of conjugated aromatic cycles.⁴⁵ In the specific case of graphite, plans of graphene are perfectly aligned and this favors electric transfer. Aromatic content and graphitization are favored by temperature, graphite being formed above 2400°C (see Figure 5). Lithium intercalation is made between the graphene sheets yielding to its good storage capacity (372 mAh/g). This reversible intercalation is usually summarized as:

Lithium diffusion is important for lithiation and delithiation processes. A well-structured phase will enable a good permeability and a good intercalation of lithium. As a general principle, the more structured carbon, the better stable lithiation capacity: up to 372 mAh/g for graphite, 220 mAh/g for carbon black (Super P)⁴⁶, 290 mAh/g for petroleum pitch (Rutgers 250 M)⁴⁷ with very disordered species but high aromatic contents. For cokes, compositions are various, initial capacities range from 500 to 800 mAh/g after treatment at 800°C but decrease below 200 mAh/g after few tens of cycles. Oxidation can improve stability around 400 mAh/g but with 200 mAh/g capacity loss during the first 20 cycles.⁴⁸ Moreover, the higher thermal treatment temperature is performed, the better is the graphitization.

Figure 5: Carbon structure evolution from mesophase depending on temperature.⁴⁹

For carbon treated at temperature up to 1000°C, the structure and the lithiation property will also depend on the precursor type, mainly soft and hard carbon with the main difference is that soft carbon can be transformed into graphite at high temperature and this is not the case of hard carbons due to a high content of structural defects. For example, soft carbons can be made from pitch at 900-1000°C. Those structures can have capacities higher than graphite as they have many structural defaults and microporosity along with small graphitic domains.^{50, 51} They however have large irreversible capacity at first cycle and high polarization between charge and discharge.⁵¹

Figure 6: Comparaison entre les différents carbones⁵²

Hard carbons are obtained from oxygen or sulfur rich precursors at temperature superior to 1000°C. Oxygen and sulfur enable partial graphitization but along with reticulation, disabling full graphitization. Typical precursors are cellulose, sucrose... Oxygen control and precursor oxygen content is rather important.

Nanosilicon (< 80 nm) is oxidized slowly from 500 °C and rapidly from 800°C.²⁹ Silicon oxidation into silicon dioxide is thermodynamically favored and exothermic ($\Delta H_{f, liq} = -902.7$ kJ/mol) and is one of the most stable form of silicon.⁶⁹

Figure 7: Thermogravimetric analysis of pure nanosilicon particles (red) and carbon coated silicon nano particles containing 60% carbon (black)⁵³

As silicon oxide capacity and also initial irreversible loss are less good than pure silicon, its oxidation should be avoided by the absence of oxygen or oxygen precursors (oxygen rich carbons) during thermal treatments. Carbon oxidation can occur earlier and independently from silicon oxidation (see thermogravimetric analysis for carbon coated Si particles in Figure 7).

To avoid oxygen, nitrogen can be used; however, nitridation of silicon from N₂ gas is also thermodynamically very favorable ($\Delta H_f = -733$ kJ/mol for the reaction $3 \text{ Si} + 2 \text{ N}_2 = \text{Si}_3\text{N}_4$) but occurs only at high temperature above 1350°C, close to silicon melting point (1410°C).⁵⁴

The temperature value has to be a compromise as higher temperature increases graphitization and improve carbon properties but, inactive SiC can be formed^{128,55,56} For instance, SiC formation has been observed at temperature as low as 800°C for petroleum pitch and polysilane.¹¹⁰ However, this low temperature is probably due to the silicon precursor reactivity. With nano silicon and pitch blends, SiC formation with 12% Si (atomic) has been observed at 1000°C.⁸³

Along with pyrolysis temperature, physical properties change; Young modulus increases up to 1000°C and then decreases: elasticity of the carbon host matrix is the worst at about 1000°C. From 1500°C, thermal and electrical conductivities both increase due to the middle and long distances graphitization process (also illustrated in Figure 8).⁴³

Figure 8: Influence of pyrolysis temperature on physical properties (E = Young modulus, λ = thermal conductivity; ρ =resistivity)⁴³

b. Pitch as precursor

Different carbon precursors have been tested⁵⁷ : graphite, PVC, pitches (coal or petroleum), PVA, PAN, PVP, phenolic resins, saccharides, and lignin⁵⁸. The most often used in academic literature are pitches and PVC. At larger scale, PVC is not used as its mass loss during pyrolysis is very high (83%) and chloride emission are generated and have to be treated.⁸³ Erreur ! Signet non défini.,⁵⁹ The interest of PVC is the good elasticity of the resulting carbons and the final Si/C composites have low specific surface areas. Pitch is a carbonaceous mixture of organic byproducts resulting from distillation of coal or petroleum, not readily useful for energy production (combustion). Its main characteristics are its high boiling points (>200°C) and its high content in aromatic molecules. Its main application is road covering, and some special grades are used as amorphous carbon coating for graphite electrodes of Li-ion devices.

During pyrolysis of pitch, hydrogen is produced due to aromatization of the molecules. It only explains a minor part of the weight loss which is due to the gasification of carbon material.⁶⁰ This usually ends between 500 and 600°C depending on the precursor. Between 350 and 450°C, polycyclic hydrocarbons of about 10 cycles face condensation reaction and their size increase^{61,62}. At temperature of 420-500°C, a liquid crystal phase called mesophase appears (cf. Figure 9).⁶⁰

Figure 9: Phase formed during thermal treatment of pitch ^{63, 62}

From temperature over 700 °C and in all cases at 900 °C, aromatics are the main molecules. Further temperature increase will mainly improve crystallinity, instead of aromaticity.⁶⁰ The pitch structure contains aliphatic and aromatic compounds in various concentrations. The C-C and C-H bond breaking during aromatization requires energy (420 kJ/mol to break an aromatic C-H bond and 325 kJ/mol for a C-H bond in a methyl group). Thus, aliphatic groups will require more energy than aromatic groups to fully decompose into aromatic cycles⁶⁰. On the other hand, the more aromatic compound, the higher the activation energy to initiate C-H bonds breaking (which is normal as those products are thermodynamically more stable).⁶³

Therefore, carbon chemistry is rather complex and difficult to characterize. In most cases, silicon will be associated with non-crystalline carbons even though some graphitic contribution can be observed. For instance, Raman spectroscopy analysis has been done on 30 nm silicon coated with carbon (19% C in weight): the spectra show two bands, the one at 1600 cm⁻¹ called G being attributed to organized graphitic carbon,⁸⁴ whereas the "D" band corresponds to disorganized carbon. This carbon is made from ethylene decomposed by a CO₂ laser.

So apparently, it is not possible to combine all the positive properties of carbon and silicon due to temperature limitations. However, various approaches have been developed to combine the most interesting properties of each, that is to say silicon capacity and carbon stability.

4. Carbon coating of silicon

Many protocols have been used to make a carbon coating on silicon, from solid precursor (mechanosynthesis), carbon dissolved in solution (sucralose, PVC...) or from gas, mainly acetylene.

a. Mechanical milling

Powders are crushed together in a high energy system with hard milling tools (usually hardened steel or tungsten carbide).^{64, Erreur ! Signet non défini.,⁶⁵} Depending on the apparatus and the targeted particle size, operating milling times range from 1 to 100 h. A temperature increase is usually observed but it remains below 200°C.⁶⁶ During crushing, two main mechanisms are encountered: pulverization which tends to form small particles,⁶⁶ and aggregation which has the opposite effect of pulverization in terms of mean particle size.⁶⁴

This method has been successfully used with various carbon precursors including graphite to obtain Si/C composites. It could be followed by thermal treatments. Coating is usually observed and irreversible capacity is decreased even though it is difficult to identify the effect of silicon particle size decrease and coating only itself^{66,67}. Despite low temperature, SiC formation has been reported for highly energetic milling process.¹⁹ Silicon particle size distribution is usually large and possible contamination by the reactor materials such as iron or tungsten, and their related carbides, can be found (up to few wt. %)^{64,68}.

b. Gas-phase synthesis

The gaseous way is advantageously a single step process as carbon is directly decomposed onto silicon particles. Acetylene is the main raw material as it is cheap, easily available, and highly exothermic (-243 kJ mol^{-1} at 900 K for the reaction $\text{C}_2\text{H}_2 = 2 \text{ C} + \text{H}_2$).⁶⁹ CVD has been used,⁷⁵ as well as PECVD (plasma enhanced chemical vapor deposition).⁷⁰

Figure 10: Scheme of plasma reactor for carbon coated silicon particles⁷¹

Acetylene decomposition starts at the temperature of 700°C .⁷² Some silicon surfaces can also catalyze this reaction and lower this temperature down to 600°C .⁷³ For homogeneity reason, it is preferable that the hot silicon particles meet the colder acetylene gas in order not to decompose acetylene alone and form carbon nanoparticles.^{29, 84}

To avoid particle handling and a step of aerosol formation, coating in line with silicon nanoparticle production is of strong interest. This has been exemplified by laser pyrolysis with two different systems: acetylene gas injection just after the silicon formation zone.⁷⁴ This method has been demonstrated at several kg/hours and electrochemical performances are shown below.

Another embodiment is the use of a second reaction zone where the flame is formed via interaction of ethylene and CO_2 laser. A radiation flame is observed.²⁹ Those approaches validate the interest of carbon coating for silicon surface protection.

Figure 11: Si@C particles obtained directly from laser pyrolysis and cycling performances obtained⁵³

c. Liquid process

This method is made in four steps:

- Carbon precursor dissolution in a solvent,
- Silicon nanoparticles dispersion in the slurry,
- Solvent removal (usually evaporation),
- Thermal treatment.

A key step is the homogeneity of dispersion of nanosilicon as agglomerates can be formed. ^{Erreur ! Signet non défini.} High shear system (Dispermat, Ultra-Turrax) can be used and, for small samples preparation, ultrasonication is the most used technique even though it should not be used with flammable solvent (cavitation can cause local temperature increase and ignite inflammation). After the solvent removal, the carbon precursor should be thermally treated to have a good protection of silicon. The effect of thermal treatment is described in the composite section.

Sucrose can be used to obtain a coating on the particles with limited success in term of stability.⁷⁵ The most complex carbon structures have been obtained through the liquid phase route using templates to create voids between silicon and carbon for instance. The idea is to have enough void to accommodate silicon particles swelling during cycling without breaking the carbon shell. This has improved significantly the silicon stability at rather high capacity values (1000 mAh/g). The preparation includes several steps, the key one being the covering of particles with a surfactant which is then covered by a silica crust. After surfactant removal, the hollow silica crust is used as a template for carbon deposition. After thermal treatment, this silica layer is removed by HF leaching.⁷⁶

Figure 12: Hollow yolk-shell structure (Si@void@C) and corresponding electrochemical performance⁷⁶

A pomegranate structure has then been obtained with “grains” of silicon inside a hollow carbon shell. Performances are also very stable with high capacities (around 700 mAh/g) for thousands of cycles, despite high irreversible losses during the very first cycle (50%).⁷⁷

Figure 13: Pomegranate assembly of Si@void@C particles and corresponding chemical performances⁷⁷

This validates the general assumption that swelling side-effects could be limited by having enough space for it. Those preparations would be difficult to scale up economically but validate that silicon can be cycled under stable conditions if the system can accommodate volume expansion. This can be done also using elastic binders in the electrode formulation.

d. Si/C composites

The previous section mainly detailed the preparation of thin carbon coating around silicon particles. Another approach is to embed silicon into a carbon matrix to form a Si/C composite. The main advantage of this approach is to obtain micrometric particles similar in size to graphite (10-40 μm) ready and easy to use. Moreover, carbon protection around silicon is much thicker and tunable^{57, 78,79}. The main routes are the liquid process (see thin coating part) with the same steps, the main difference being the higher carbon content. For some precursor, especially pitches, it is possible to take advantage of the low temperature melting point to disperse silicon into hot fused carbon, before a thermal step. During solvent evaporation and thermal treatment, some micropores can be created, thus increasing specific surface area and, therefore, irreversible capacity.⁷⁸ Moreover graphite and some other additives can be added in the composite to enhance properties (electronic conductivity, stability,...) This method can for instance yield Si/C/Graphite composite with specific capacity of 80% after 100 cycles with 17 wt.% Si and a current density of 130 mA/g.^{57,60,85} The carbon matrix act as an intermediate between electrolyte and Si nanoparticles. It avoids direct contact between them and creates a chemically and mechanically stable SEI.^{80,81 82, 19}

A key step for hybridization is the thermal treatment and it is developed here using pitches as carbon precursors.

*Figure 14: SEM image of a Si-C composite from PVC precursor (clear particles are silicon)*⁸³

Various precursors can be used. One important feature is the mass loss during thermal treatment. At 900 °C, some precursors have very large mass losses (from more than 90 % for cellulose and sucrose, down to 44% for some pitch) which makes them difficult to use due to the large gas treatment/energy recovery unit which has to be implemented:

Among other criteria, the aromatic content of the pitch is interesting as it will favor crystalline carbon. Oxygen content is important as high content will favor the reticulation and the formation of hard carbons. Silicon in carbon matrix is well documented.^{Erreur ! Signet non défini.84,19,65,85,86,87} Carbon matrix enable ionic and electric conductivities and helps to form a more stable SEI.^{19,65}

Initial coulombic efficiencies (ICE) of Si/C composites are very variable. PVC and pitches as precursors coupled with nano-silicon have the highest values (78-80%)^{59,88, 85} Lignin yield to lower coulombic efficiency due to its higher oxygen content (71.6 % ICE)⁸³.

A good summary of all those approaches have been made by combining several of them. Hu et al. have mixed nano-silicon particles with micrometric graphite and CMC as binder. The blend is then dried and pyrolyzed at 900°C: silicon nanoparticles cover the graphite surface.⁸⁹ Then, pitch dissolved in THF is added and pyrolyzed at 900°C: a pitch-based carbon layer is formed around the silicon on graphite particles. Then, the particles are placed in a CVD equipment and a carbon layer coming from acetylene decomposition at 700°C is deposited on the particles to form graphite@Si-C_{ex}-CMC@C_{ex}-pitch@C_{ex}-CVD. Those complex particles have carbon coming from 4 different sources and forming four successively layers, one of them containing also silicon. Liquid and gaseous processes are used (we can note that the first Si-graphite mixing could have been done by powder mixing). This material has a first discharge capacity of 762 mAh/g and then the capacity stabilized around 600 mAh/g from cycle 80 to 140. This demonstrates that very good electrochemical performances can be obtained with silicon and complex carbon structure/texture. The challenge now is to obtain very good electrochemical performances with more simple structure and this implies a good knowledge of carbon and silicon chemistries.

5. Conclusion

Silicon has a very high specific capacity for Li-ion batteries anodes (3579 mA h g⁻¹ based on the Li₁₅Si₄ formation) and do not form dendrites, which is a strong advantage over lithium, the other potential high capacity anode material. Silicon has two disadvantages: cracking during electrochemical cycling, which can be solved by using particles smaller than 150 nm; and limited cycling stability due to the continuous formation of SEI (solid electrolyte Interphase). SEI is due to silicon surfaces reaction with electrolyte. Those reactions are limited with carbon, especially graphite, but carbon-based material have capacities limited to 372 mA h g⁻¹. Silicon nanoparticles hybridization with carbon can benefit from both interests: high silicon capacity and high carbon stability. This can be made possible by making a carbon shell around the silicon. Formation of silicon carbide should be avoided and, therefore, limits the type of carbon to “coke” that can be obtained below 1000 °C. Various ways have been tested: solid, liquid and gaseous carbon precursors, usually followed by a thermal treatment to increase carbon crystallinity. Simple coating and complex structure (carbon hollow structure around Si, pomegranate) have been demonstrated at laboratory scales. Very good performances can be obtained with silicon and complex structure. It validates some principles to improve silicon stability: use Si particles with diameter below 150 nm, protect the silicon surface with a carbon coating and enabling swelling without electrode cracking. One challenge for academic studies is to increase the overall active material stability. For larger use, the challenge now is to obtain very good performances with simple and cheap structure and this implies a good knowledge of both carbon and silicon chemistries.

Direct carbon coating techniques in line with silicon particles synthesis seems to be the most efficient way, among them laser pyrolysis has demonstrated large scale capacities. Integration of nano-silicon in carbon matrix is also simple and exhibit good results, especially when using pitch as carbon precursors.

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