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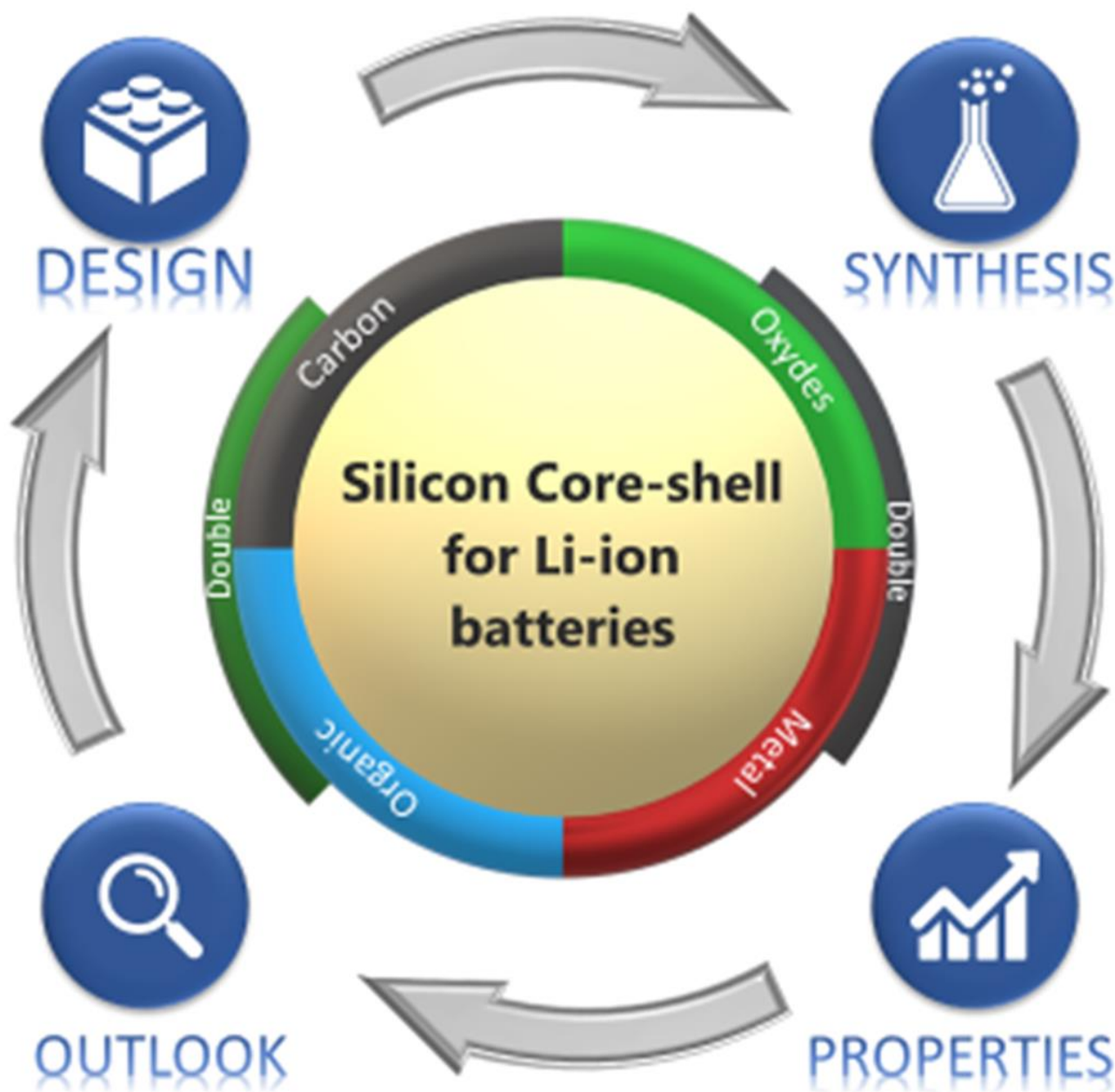


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## Engineering of silicon core-shell structures for Li-ion anodes

Bastien Rage<sup>[a]</sup>, Diane Delbague<sup>[b]</sup>, Nicolas Louvain<sup>[a,c]</sup> and Pierre-Emmanuel Lippens<sup>[a,c]</sup>

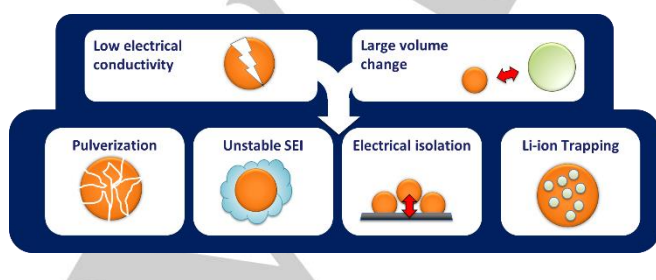


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**Abstract:** The amount of silicon in anode materials for Li-ion batteries is still limited by the huge volume changes during charge-discharge cycles. Such changes lead to the loss of electrical contacts, as well as mechanical and surface electrolyte interphase (SEI) instabilities, strongly reducing the cycle life. Core-shell structures have attracted a vast research interest due to the possibility of modifying some properties with a judicious choice of the shell. It is, for example, possible to improve the electronic conductivity and ionic diffusion, or buffer volume variations. This minireview gives a comprehensive overview of the recent developments and the different strategies used for the design, synthesis and electrochemical performance of silicon-based core-shells. It is based on a selection of the main types of silicon coatings reported in the literature, including carbon, inorganic, organic and double-layer coatings. Finally, a summary of the advantages and drawbacks of these different types of core-shells as anode materials for Li-ion batteries and some insightful suggestions in regards to their use are provided.

## 1. Introduction

The constant growth of our society, its demands, and its impact are today one of the most urgent matter that research must work on. It is believed that our electricity consumption will go up by more of 70% between 2013 and 2040.<sup>[1]</sup> The electricity production worldwide is still vastly relying on fossil energy, meaning that our energy consumption will affect more and more climate change. Other ways exist, but their uses are still slowed by major drawbacks, such as rate and time of production. It is well known that energy storage systems are still lacking in a grand scale. Though batteries have progressed quite well since the beginning of the Li-ion era, the basic cell architecture is still as it was in the late 90s.<sup>[2,3]</sup> The incremental innovations are approaching their limits in terms of energy density, and thus a radical change in architecture is needed to work toward more space and weight-efficient systems.



**Figure 1.** Summary of the problematics linked to silicon lithiation and their resulting issues.

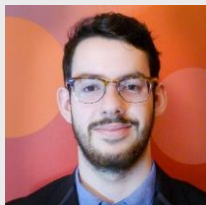
Silicon was revealed as an interesting candidate to upgrade the Li-ion systems for decades due to its high capacity ( $4200 \text{ mAh.g}^{-1}$  and  $2400 \text{ mAh.cm}^{-3}$ ), its appreciable voltage plateau ( $0.1\text{--}0.3 \text{ V vs Li/Li}^+$ ), its low toxicity and Earth's crust abundance.<sup>[4,5]</sup> But the severe drawbacks of using a silicon based negative electrode still haven't found answers (figure 1).<sup>[6]</sup> The most severe intrinsic problem is the volumetric expansion of silicon during the lithiation of the particles due to Li-Si alloying reactions. This leads to cracking, pulverization, and isolation of silicon particles in the electrodes. It also means that the solid electrolyte interphase (SEI) is unstable, and therefore "ever-growing".<sup>[7]</sup> It is important to note that the use of nanoparticles of silicon have been generalized, as it is granted that under  $150 \text{ nm}$  of diameter, pulverization does not occur and the SEI is much more stable.<sup>[8,9]</sup> However, such a small particle size increases the surface area, which leads to more SEI formation, and volume expansion is still present. The cost of Si nanoparticles is very much higher than that of Si microparticles. However, this cost is bound to decrease sharply. Those particles find more and more applications, in sectors such as optoelectronic, photocatalysis and obviously energy storage. And as the number of usages rises, the synthesis methods are becoming much more diverse and studied, and thus less expensive.<sup>[10]</sup>

Using a core-shell structure is highlighted as a solution for the past twenty years to resolve the mechanical, electrical and chemical problems.<sup>[11]</sup> It is expected that the shell will help improve the structural stability of the silicon core during cycling, while also stabilizing the SEI by limiting the contact between the silicon particle and the electrolyte. In addition, the coating could help with other drawbacks such as the low conductivity or contact loss, depending on the material used. Carbon coatings have been the first implemented, as they are widely known and easy to synthesize, but today researchers have been more and more creative, leading to some more complex and attractive core-shell materials.<sup>[12,13]</sup> Many impressive works have reviewed silicon based anodes,<sup>[14–16]</sup> including topics such as carbon buffering,<sup>[17]</sup> nanostructuring,<sup>[18]</sup> or overall architecture.<sup>[19]</sup> In this work, we focus on the engineering of one or multiple shells over silicon particles and the resulting improvements of the electrochemical performance. By selecting some representative examples of core-shells, we will cover different technics to synthesize such particles, describe their main structural and morphological features, show how these features can change the properties of the Si-based anodes for Li-ion batteries, and indicate in our conclusions what an optimal architecture could look like. This work is structured around the nature of the shell, as it is the starting point of most of the research works featured and is representative of the design performance. Section 2 will concern carbon coatings, vastly studied since they can easily be obtained, via a wide array of synthesis, and improve electronic conductivity and cycling

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stability of the material. Because such coatings are not mechanically strong and also induce high losses in capacity over the first cycles, inorganic shells are discussed in section 3. Their mechanical toughness is appreciated to manage the volumetric expansion, while depending on the compound, electronic and/or ionic conductivity is greatly enhanced. However the small but constant capacity fade during long-term operation, leads to the study of coatings that would not constrain, but accept the volume expansion of Li-Si alloying reactions, hence section 4 covers organic coatings. Their elasticity and resilience help keep the interface integrity, the materials showing stability over a high number of cycles, yet prejudiced by high losses at early stages and often complicated synthesis methods. As all types of shells bring their share of good and bad points, combining two shells is a solution to try to obtain synergetic effects. Section 5 will focus on those double-shell structures, showing it is indeed possible to reduce the drawbacks linked to the nature of one shell by adding another.

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Nicolas Louvain is Associate Professor at the University of Montpellier, working on Li-ion materials modification and advanced *operando* characterization techniques at ICGM. He developed the atomic layer fluorination method, an innovative way of using F atom and surface chemical bonding to improve the electrode reactivity during cycling.



Pierre-Emmanuel Lippens is Director of research CNRS at ICGM, working on electrode materials for alkali-ion batteries and electrochemical mechanisms by combining experimental and theoretical techniques.



## 2. Carbon coatings

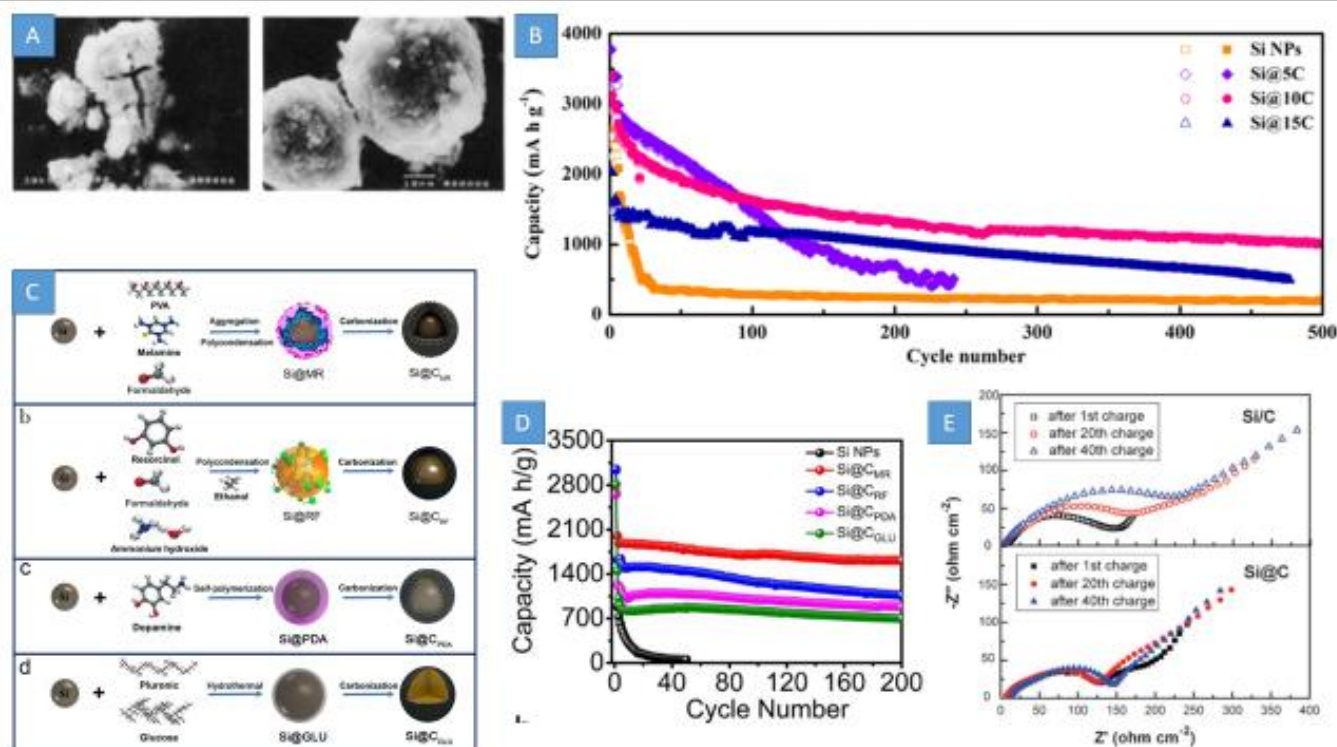
Carbon was the first coating studied on silicon to be used as anode material for Li-ion batteries.<sup>[12]</sup> At the time, carbon was already a well-known material for negative electrode of such batteries.<sup>[3,20]</sup> Indeed, it was used early as a commercial electrode, and thus the behavior of graphitic carbon at the negative electrode was already thoroughly studied. However, in a core-shell structure, the carbon coating, which must fully wrap the particle, is more than often poorly organized. Yoshio et al., before their work on silicon, to reduce the SEI in graphitic anodes, studied it.<sup>[21]</sup> Carbon is a good electrical conductor,<sup>[22]</sup> has good elasticity and is easy to synthesize.<sup>[23,24]</sup> It is also cost-friendly and might be bio-sourced. However, the nature, thickness and purity of the coating will greatly affect the final material properties and should be chosen adequately. The silicon-carbon core-shells are expected to have a more stable SEI, a more stable structure and of course a better electronic conductivity. These improvements can be related to the properties of the carbon shell as discussed in this section from some selected examples.

The works of N. Dimov et al. furtherly proved that carbon is indeed a good candidate to make silicon more relevant in Li-ion batteries as soon as 2001.<sup>[12,25,26]</sup> The carbon coating resulting in silicon-carbon core-shells was made by thermal vapor deposition of benzene. Such a synthesis results in disordered graphite coated over micron-sized silicon. The authors obtained particles of 5 to 10  $\mu\text{m}$  of average diameter, way over the starting 1 to 2  $\mu\text{m}$  of the uncoated silicon particles, showing a thick carbon coating was realized. A stable capacity of around 800  $\text{mAh}\cdot\text{g}^{-1}$  was obtained over at least 30 cycles, which is an improvement over uncoated silicon anodes. It was indeed able to accommodate the expansion for some time (see figure 2a). However, the lack of stability in the long run, as well as the low capacity (in respect to the theoretical capacity of silicon), imply that more optimization is needed. Indeed, the coating is thick and crude in those studies and the carbon does not exhibit any particular characteristics. Those early works also suggest that better performances require core-shell nanoparticles instead of carbon coated silicon micro-sized particles.

After those three groundbreaking works, the following studies would mostly focus on Si based nanomaterials, under 100 nm in diameter. Those particles are not prone to pulverization and would also reduce the strain on the coating.<sup>[8]</sup> Shortly after the work of Dimov et al., Ng et al. tried to improve the carbon coating efficiently by working with another synthesis medium.<sup>[27]</sup> They used spray pyrolysis with Si nanoparticles (80 nm) diluted in citric acid and ethanol. The amorphous carbon coating obtained was relatively constant in thickness at around 10 nm, meaning that 44 wt% of the composite was still silicon. The capacity is higher than the previous works, with a first discharge of 2600  $\text{mAh}\cdot\text{g}^{-1}$ . After the 20<sup>th</sup> cycle, this material still showed a capacity of approximately 1500  $\text{mAh}\cdot\text{g}^{-1}$ . Ng et al. hereby showed the beneficial effects of a carbon coating, providing dimensional stability for the electrode. It is however, counterbalanced by a lower initial coulombic efficiency (ICE), due to the lithium insertion properties of amorphous carbons.

In 2016, the effect of the coating thickness was studied in more depth, using a tunable sol-gel synthesis.<sup>[28]</sup> Resorcinol-

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**Figure 2.** a) SEM pictures of Si (left) and Si@C core-shell (right) after cycling.<sup>[12]</sup> b) Cycling performance of Si nanoparticles and Si@C core-shells of different layer thicknesses (5, 10 and 15 nm) at 0.5 A.g<sup>-1</sup>. c) Schematic illustration of the preparation of different Si@C core-shells from different precursors. d) Associated cycling performances of said Si@C core-shells vs bare-Si precursor at 0.4 A.g<sup>-1</sup>. e) EIS spectra of Si@C composite (up) and core-shell (below) after the n<sup>th</sup> cycle and at 1.2 V vs Li/Li<sup>+</sup>. Reproduced with permission from ref. [12] (a). Copyright 2001, CSJ Journals; ref. [28] (b). Copyright 2016, Elsevier; ref. [34] (c,d). Copyright 2020, American Chemical society; ref. [35] (e). Copyright 2009, Royal Society of Chemistry.

formaldehyde resin (RF) was polymerized on the surface of the Si nanoparticles, before being carbonized. By modifying the amount of polymer precursor, the thickness of the carbon layer could be tailored. Si nanoparticles with diameter of 80 nm and coating thickness ranging from 2 to 25 nm were compared. The electrochemical results of those materials indicate that the optimal thickness for this silicon precursor should be around 10 nm (see figure 2b). Indeed, a thinner shell would lead to rapid capacity loss, surely linked by the destruction of said shell, and return to a more classic silicon anode behavior. A thicker coating, however, shows no improvement on stability, but lowers the specific capacity by adding unnecessary weight. The core-shell with the 10 nm coating thickness showed impressive electrochemical performance with a capacity of 1006 mAh.g<sup>-1</sup> and a coulombic efficiency over 99.5% after 500 cycles. Xiao et al. proved that over a certain thickness, the compressive stress of the shell would also limit the capacity of the particles, by complicating the Li<sup>+</sup> ion diffusion.<sup>[29]</sup> This article shows that proper optimization is needed to bring out the improvements given by such a coating. However, it is also important to remember that the optimal thickness given here is only true for their system, as for another precursor or carbon coating, the optimal solution would surely be different.

It is important to control the shell size in such materials, but the nature of the carbon seems to strongly impact the electrochemical performance. A lot of different carbonated precursors have been studied, such as PVDF,<sup>[30]</sup> phenolic resin,<sup>[31]</sup> glucose<sup>[32]</sup> or pre-doped gel.<sup>[33]</sup> It is generally accepted that the structure, dopants, porosity and surface area of carbon

would define the functioning of the Si@C core-shells. Ma et al. studied four different shell precursors, before highlighting the most efficient one (see figure 2c).<sup>[34]</sup> The four polymers, but also the four synthesis processes, were of different natures: melanine resin formed by aggregation and polycondensation (CMR), RF resin by polycondensation (CRF), polydopamine by self-polymerisation (CPDA) and glucose by hydrothermal synthesis (CGLU). Apart from the glucose-based materials, the thickness of the shell is roughly 50 nm. The overall stability is the same for all core-shells, however the capacities of the four materials are different. If all four have a first discharge between 2800 and 3200 mAh.g<sup>-1</sup>, after 200 cycles, the CMR boasts an impressive value of 1614 mAh.g<sup>-1</sup> at a current of 400 mA.g<sup>-1</sup> (figure 2d). In comparison, the three other samples would only be at 1064, 880 and 700 mAh.g<sup>-1</sup> for CRF, CPDA and CGLU, respectively. Electrochemical testing also shows that the difference is made during the first 5 cycles, as after that the curves are roughly parallel, apart for CRF, which is losing capacity a little bit quicker. The structure and nature of the different carbon coatings are then thoroughly studied, by Raman and infrared spectroscopies, Brunauer-Emmett-Teller surface analysis (BET), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), while X-ray photoemission spectroscopy (XPS) was only used for the CMR compound. Thanks to those analyses, the better behavior of CMR is linked directly to four characteristics: the disorder of the carbon structure, the presence of heteroatoms, a higher porosity and a good sealing of the silicon. Other researchers, concluding in the same manner, have pointed those factors also.<sup>[28,29,35]</sup> Tendencies can be extracted from those

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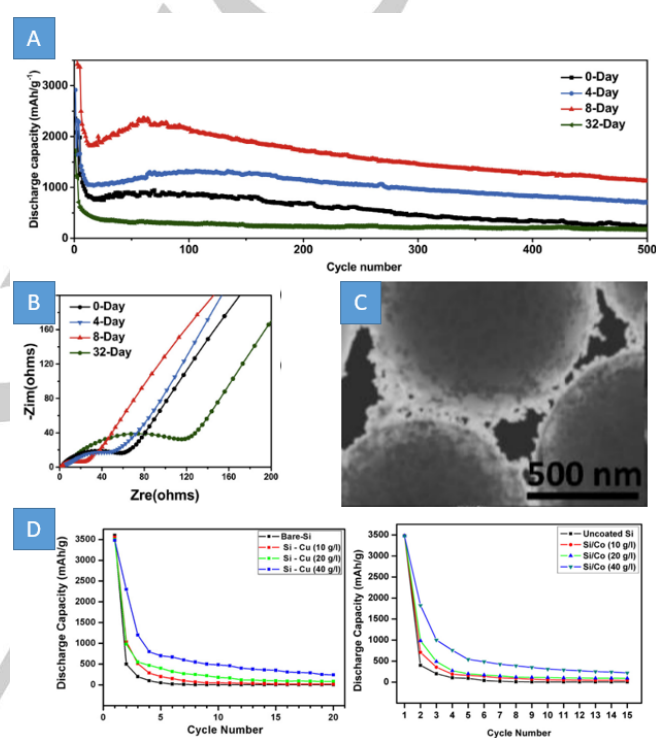
articles: (i) a more disordered structure, related to a more amorphous carbon, is shown to behave better during electrochemical cycling; (ii) heteroatoms in the carbon shell enhance the cycling behavior by improving the electronic conductivity of the coating and (iii) increase the mechanical strength; (iv) the amorphous carbon doped with heteroatoms will most likely be slightly more porous. The latter is a double-edged sword, as more porosity means more void to accommodate the expansion, but also more surface for the SEI to grow and the electrolyte to degrade itself.

The complex nature of the core-shell architecture often requires accordingly complex synthesis methods. If the processes are not expensive, the majority of them are not suitable for sustained commercial production. In addition, they rely on a nano-silicon powder precursor, a costly material. It is however possible to find alternatives, as proposed by Sourice et al.<sup>[36,37]</sup> They introduced an innovative process relying on a double-staged LCVP setup. While the set-up might be expensive, it is perfectly tailored for sustained production, as the precursors are cheap gases ( $C_2H_4$  and  $SiH_4$ ). This method gives core-shell particles constituted of a 30 nm diameter silicon core, with a coating of disordered carbon (Raman intensity ratio  $I_D/I_G \sim 1.0$ ) that is controllable in thickness (2.5 or 0.7 nm). One other benefit of this synthesis approach is to reduce the amount of native oxide on the Si surface, which is irreversibly transformed in Si during the first cycle, by protecting the silicon surface directly by carbon as shown by XPS. Electrochemical tests for electrodes composed of 50 wt% of active material, 25 wt% of carbon filler and 25 wt% of CMC binder show real promises. They show a capacity for the formulated electrode moving from  $700 \text{ mAh}\cdot\text{g}^{-1}$  to  $500 \text{ mAh}\cdot\text{g}^{-1}$  in 500 cycles at a current rate of 2C. This material outqualifies graphite in terms of capacity, but also seems to allow higher current rates. Once again the carbon shell proves it is worth stabilizing the structure and SEI of the electrode by limiting the contacts between the silicon cores and the electrolyte according to the authors.

Carbon coatings are very diverse, and have been studied thoroughly during the last 20 years. The improvements over bare silicon and carbon composites are there (see figure 2e). The gains in stability during cycling have been widely observed, and have been attributed to the protective effects of the carbon shell. This shell limits the contact between the silicon particle surface and the electrolyte, but also helps keeping the integrity of said particle during cycling. In most works, better conductivity is also shown for the core-shell structures. However, after all those works, some limitations tend to appear as even the most optimized structures are not fully mature for commercial use as primary component at the anode. The irreversible loss at the first cycle is excessively high for Si@C core-shells and is most of the time higher than that of bare Si nanoparticles. This behavior is explained by the nature of the carbon SEI and the porosity of its surface. In addition, the overall stability of anodes with a high percentage of Si is still too low. The majority of reported Si@C based anodes only retain half of their starting capacity after 100 cycles, if they manage to hold until then. This means that after some time, the coating will break and the various drawbacks of silicon start appearing again. Thus, alternative inorganic shells were suggested to overcome these drawbacks, because of their toughness and chemical stability.

## 3. Inorganic coatings

Contrary to carbon, inorganic coatings are more diversified in term of chemical nature. With better mechanical properties over carbon, those materials maintain the shell stable longer and even constrain the silicon core more efficiently during charge-discharge cycles. The vast choice of inorganic compounds means also that seeking other improvements is possible such as ionic or electronic conductivity. As shown in this section, the silicon surface oxidation that can even be natively formed improves the stability of the SEI, while a purely metallic shell enhances the electronic conductivity, other oxides can be ionic conductors and nitrides can be extremely tough.



**Figure 3.** a) Electrochemical cycling tests of various Si@SiO<sub>x</sub>/SiOH nanoparticles with different thicknesses of surface amorphous layer ( $100 \text{ mA}\cdot\text{g}^{-1}$  for 3 cycles and  $1 \text{ A}\cdot\text{g}^{-1}$  afterward) and b) associated EIS spectra at the end of the second charge. c) STEM dark field image of Cu-coated silicon particles. d) Electrochemical cycling tests of Si@Cu (left) and Si@Co (right) core-shells at  $100 \text{ mA}\cdot\text{g}^{-1}$ . Reproduced with permission from ref. [38] (a,b). Copyright 2020, Elsevier; ref. [43] (c). Copyright 2012, American Chemical Society; ref. [42] and ref. [46] (d). Copyright 2014, Elsevier.

It was recently shown that the amorphous native oxide coating around the Si nanoparticles would also have a tremendous effect on the electrochemical behavior.<sup>[38]</sup> By simply immersing the particles (stripped of their native oxide by etching beforehand) into a water/ethanol solution, Guo et al. managed to control the thickness and the composition of the oxide layer. Though the layer thickness resulting of such treatment is relatively small, at 2.8 nm even after 32 days, the effects are impressive. The 8-day sample, with a shell of 2 nm of SiO<sub>x</sub> and SiOH, has a higher capacity than that of bare Si nanoparticles, but also a better stability (figure 3a). It retains 45% of its capacity after 500 cycles.

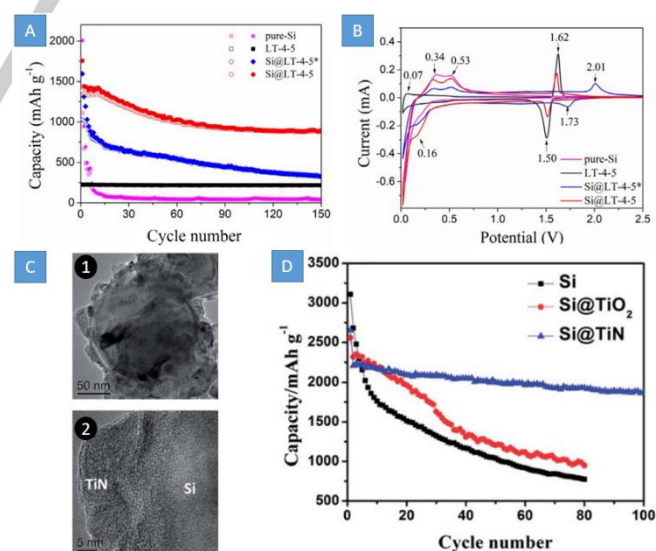
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The authors suggested that the small oxide layer provides a more stable SEI, by producing lithium silicate and lithium oxide during the first lithiation. In addition, SiOH groups on the surface help create better connections with both the conduction agent and the binder. However, after 32 days, the oxide layer has reorganized into SiO<sub>2</sub>, showing bad electrochemical characteristics (figure 3b). The justification is that SiO<sub>2</sub> layer is lithiated into Li<sub>4</sub>SiO<sub>4</sub> that has a volumetric expansion of around 200%, thus cracking rapidly, exposing new and fresh silicon surface leading to new SEI. Another possibility is that the high electrical resistivity of SiO<sub>2</sub> makes it impossible to fully lithiate the silicon particles, hence the low starting capacity. Novikov et al. explained this behavior differently, showing that the degradation of the electrolyte is different on SiO<sub>2</sub>, and that the buildup of LiF and lithium phosphate leads to the loss of contact of the particles.<sup>[39]</sup> Kong et al. studied also the effect of crystallinity in such systems.<sup>[40]</sup> By varying the annealing temperature of the material, they modified the crystallinity and studied the resulting properties. This work highlights the importance of the crystalline state of the SiO<sub>x</sub> layer. Electrochemical impedance spectroscopy (EIS) shows the increase of resistivity as crystallinity increases, and the decrease of electrochemical performance. Once again, the presence of some oxides on the surface of silicon improves the cyclability until a certain thickness and crystallinity.

Metal coatings have also been thought as electron conductive layer around silicon. The metallic shell should conduct Li<sup>+</sup> ions through without reacting with both lithium and the electrolyte. However, to conduct Li<sup>+</sup> ions, the coating has to be uneven, as the ionic diffusion is done at grain boundaries.<sup>[41]</sup> Those characteristics heavily limit the possible choices of synthesis and elements. There are different reports about copper coating by T. Cetinkaya et al. and S. Murugesan et al., adapting an idea already used in silicon systems to improve stability and conductivity.<sup>[42–45]</sup> Their synthesis led to the growth of very small Cu particles, covering uniformly the silicon micro-sized particles (figure 3c). By staying at low temperature, there is few to no CuSi alloys in the material as shown by X-Ray diffraction (XRD). However, both studies resulted in poor improvement over bare-Si, even if it is to be noted that they studied those coatings over micro-scale Si particles. Murugesan et al. electrochemical tests show a low capacity compared to the one awaited for the loading of their electrodes. In the synthesis proposed by Cetenkaya et al., copper particles are grown on the surface of micro-scale Si particles by electroless deposition with palladium as a medium. The obtained copper coating, of about 100 nm, is thicker than that obtained by Murugesan et al. but the improvements on the capacity retention are also small, mostly due to the size of the Si particles and the relatively thin coating (figure 3d). The same group obtain similar results for cobalt coating, with the same synthesis method.<sup>[46]</sup> The metallic coating increases the conductivity of the electrodes, as shown by the EIS spectra in all those articles, and alleviates a little the volumetric expansion, that much is proven. But the effects in the battery lifetime are all but proven, as coating on micron-sized silicon obviously breaks quickly. The improvements in stability might only be due to the diminution of silicon relative quantity in the electrode. A more recent study by Hou et al. of copper coated silicon nanoparticles, showed more promising performance, greatly improving electronic conductivity and cycling stability.<sup>[47]</sup> Multiple points

however are yet to be explored and explained as the authors added a further carbon coating and focused on this double-layer material.

Metal oxide shells have been more successful. They have the advantages of simpler synthesis, lower density and higher porosity. Intrinsically, they would bring rather good ionic conductivity, as well as good mechanical properties. Oxides such as LiAlO<sub>2</sub> have been synthesized as coating on silicon nanoparticles,<sup>[48]</sup> but were also proven efficient for cathodes.<sup>[49,50]</sup> In the work of Q. Ai et al., a shell of Al<sub>2</sub>O<sub>3</sub> was first placed. This layer was then lithiated in a tubular oven with lithium hydroxide monohydrate. The final LiAlO<sub>2</sub> shell is 2 nm thick, over the 100 nm wide Si nanoparticles. The authors studied and observed the coating by XRD, SEM, high-resolution TEM and energy dispersive spectroscopy (EDS), showing the uniformity of the shell and the increasing thickness with the time of synthesis. The overall electrochemical capabilities are impressive, with a perfect stability on 100 cycles at 2000 mAh.g<sup>-1</sup>, but after a 33% capacity loss at the first lithiation. Those good properties were explained as being due to two effects of the LiAlO<sub>2</sub> shell. First, the nature of the shell itself, thanks to its good ionic conduction, helps to fully lithiate and amorphize the silicon particles. The second and crucial aspect is that the LiAlO<sub>2</sub> shell prevents the decomposition of the electrolyte, providing a stable SEI. Overall, the obtained material is an improvement over bare-Si, both in stability and rate capacity. Obviously, other compounds have been studied, but the most notable ones are TiO<sub>2</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO). Those are usually used directly as active materials in highly stable, but low capacity, electrodes. In multiple works they are coated around silicon nanoparticles, in different structures and thicknesses. Early works using crystalline materials gave rather poor electrochemical performance.<sup>[51,52]</sup> However, J. Yang et al., in



**Figure 4.** a) Electrochemical cycling tests of Si nanoparticles, LTO and two different Si@LTO core-shells at 0.5 A.g<sup>-1</sup>. b) CV curves of the same materials at a rate of 0.1 mV.s<sup>-1</sup> between 0.01 V and 2.5 V. c) TEM picture of Si@TiN core-shell (1) and HR-TEM of the same sample (2). d) Electrochemical cycling tests of Si nanoparticles, Si@TiO<sub>2</sub> core-shell and Si@TiN core-shell at 0.1 C. Reproduced with permission from ref. [54] (a,b). Copyright 2020, Elsevier; Ref. [55] (c,d). Copyright 2014, Royal Society of Chemistry

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2017, published interesting results about amorphous  $\text{TiO}_2$  coated Si nanoparticles.<sup>[53]</sup> Via a simple sol-gel synthesis, they obtained a 3 nm shell of amorphous titanate oxide on their 100 nm silicon particles. The coating was characterized by XPS and TEM/EDS, showing the presence of Ti-O bonds, while the XRD patterns did not reveal signs of crystalline  $\text{TiO}_2$ . As proved by cyclic voltammetry, the amorphous coating shows no sign of lithiation during cycling, but the overall material is a great upgrade over crystalline  $\text{TiO}_2$  in term of electrochemical performance. The coating leads to a decrease of the charge transfer resistance, but also the elasticity keeps the shell intact during cycling, thus keeping the electrolyte away from the Si core. LTO deposition has also shown interesting features, as proved by Liu et al.<sup>[54]</sup> Thanks to a self-assembly reaction and a further calcination, they obtain a rugged shell of LTO. The final particles have a shell thickness of 30 nm of crystalline and porous LTO as shown by TEM, XRD and BET curves. The synthesized shell has also Li-storing capabilities, expressing a stable capacity of around  $250 \text{ mAh.g}^{-1}$  (figures 4a, 4b). The LTO coated Si particles exhibit good electrochemical properties, having a relatively stable capacity over 150 cycles, finishing at  $1000 \text{ mAh.g}^{-1}$  after a first lithiation of  $1750 \text{ mAh.g}^{-1}$  (Figure 4a). Once again, the metal oxide coating improves the ionic conductivity, as well as buffers the volumetric expansion.

Tang et al. synthesized Si core-shell nanoparticles with titanium nitride as coating, a compound renowned for its hardness.<sup>[55]</sup> As Si-TiN composites have shown promising electrochemical performance, the authors decided to reduce as much as possible the inactive fraction of the material, hence the core-shell structure. It was achieved by annealing a preliminary  $\text{TiO}_2$  coating in a nitrogen atmosphere (figure 4c). The crystallinity and the presence of TiN was proven by XRD, TEM/EDS and XPS. The obtained material has tremendous electrochemical properties with more than  $2000 \text{ mAh.g}^{-1}$  over 150 cycles (figure 4d), but also good rate-capabilities. The improvements over both bare-Si and Si@ $\text{TiO}_2$  core-shells are obvious. The authors attribute those gains to enhanced conductivity, structural stability and SEI stability. The study indeed shows that the morphology of the particles does not change much during cycling, confirming the sturdiness of the TiN shell that constrains the Li-Si alloying reactions. TEM images and EIS spectra are, in fact, similar at the 1<sup>st</sup> and 30<sup>th</sup> cycles. This work proves that a hard ceramic material such as TiN can be used as a shell to improve stability and rate capacity of Si nanoparticles during cycling.

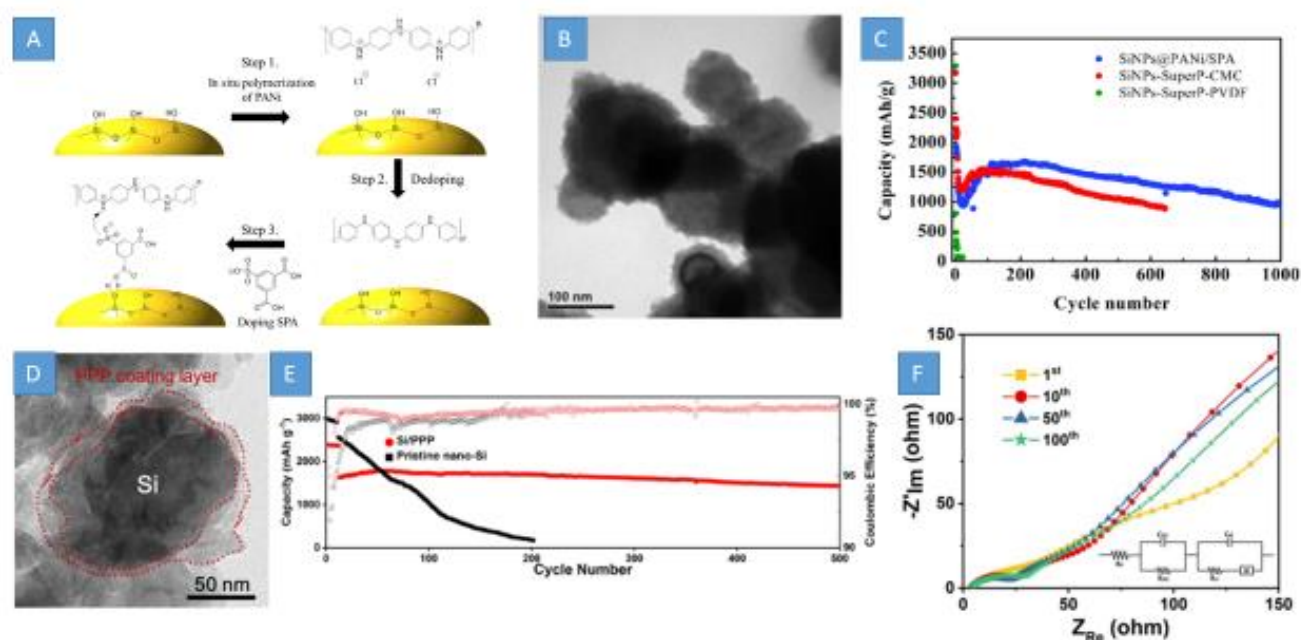
Overall, inorganic shells have given mixed results. Coatings made of oxides and nitrides tend to show good results, while purely metallic shells were underwhelming. For the latter, they showed little to no improvement on bare-Si microparticles but recent results indicate possible improvements for nanoparticles. Metallic shells would surely improve the electron conductivity but, depending on their structure, would be impermeable to Li ion, rendering access to the silicon core harder and thus reducing drastically rate capabilities. Oxides bring many more benefits: the capacity retention is enhanced, the rate capability tends to improve, and the ICE is mostly higher. However, in most cases, a real stability is never attained as the capacity keeps decreasing cycle after cycle. Also, the shell thickness must be controlled

perfectly. A too thick shell would lead to isolating silicon particles and constraining them, lowering both rate capabilities and specific capacities. A too thin shell does not show significant improvements, and the shell might break quickly, leading to rapid decay of the electrode capacity. In conclusion, although those species improve the overall electrode characteristics, the resulting materials are still not stable enough in the long run. The constant stress on the shell will slowly but surely lead to capacity losses, and it shows by a constant capacity fade. The study of organic compounds as a shell can help in that case, as they will keep their integrity during cycling and not constrain silicon.

#### 4. Organic coatings

Another way of working the problem would be to not restrain the expansion but accommodate it. The flexibility given by polymeric materials would help keep the integrity of the electrode and buffer a little the strain. However, most organic compounds are not that stable (be it against electrolytes, lithium, or voltage) and most of them are insulators. Another issue is to link the polymer to the silicon particle. Though OH bonds can be easily made, they are usually not resistant. Finding suitable candidates is thus obviously difficult. Several groups studied silicon particles embedded inside a conductive polymer matrix or a material more akin to composites.<sup>[56–59]</sup> Recently, different papers have shown that realizing true core-shell particles is possible, adding a new dimension to the thematic. For example, including silicon in a conductive and flexible matrix made of polymer such as PANi would reduce the resistivity of the electrode brought by the used insulator binder. Also using a conductive organic coating would ensure that the shell would not break and keep separating the electrode and electrolyte during cycling. As most polymer are insulator, it is also theorized that a semi-carbonized organic material could combine electronic conduction and keep its flexibility. These different aspects are discussed in the present section.

Conductive polymers are the obvious choice in this case and as such, polyaniline (PANi) coatings have been studied by several groups.<sup>[58,60,61]</sup> H. Lin et al. brought it further, this time focusing on an all organic approach, and broadening the possibilities to the electrode formulation.<sup>[62]</sup> In their work, they used PANi as coating on Si nanoparticles and 5-sulfoisophthalic acid (SPA) as a dopant. The latter forms hydrogen bonds with the hydroxyl groups at the silicon surface and the amine groups of PANi, creating what they call a bridge between the coating and the particles (figure 5a). The PANi coating is formed by self-polymerization of aniline in solution, followed by the removing of chloride with help of a NaOH solution. After adding the SPA dopant, the slurry formed is directly casted onto copper, without any need of binder and/or extra-carbon. The particles are fully coated by the polymer, showing a rough surface on the TEM pictures (figure 5b), homogeneously distributed within the electrode and of porous nature as shown by SEM. The dopant not only modifies the structure and bonding of the material, but also enhances the conductivity thanks to sulfonic acid groups ( $-\text{SO}_3\text{H}$ ), which is thrice that of the chloride doped one. The capacity retention is quite impressive, as it retains more than 80% of its



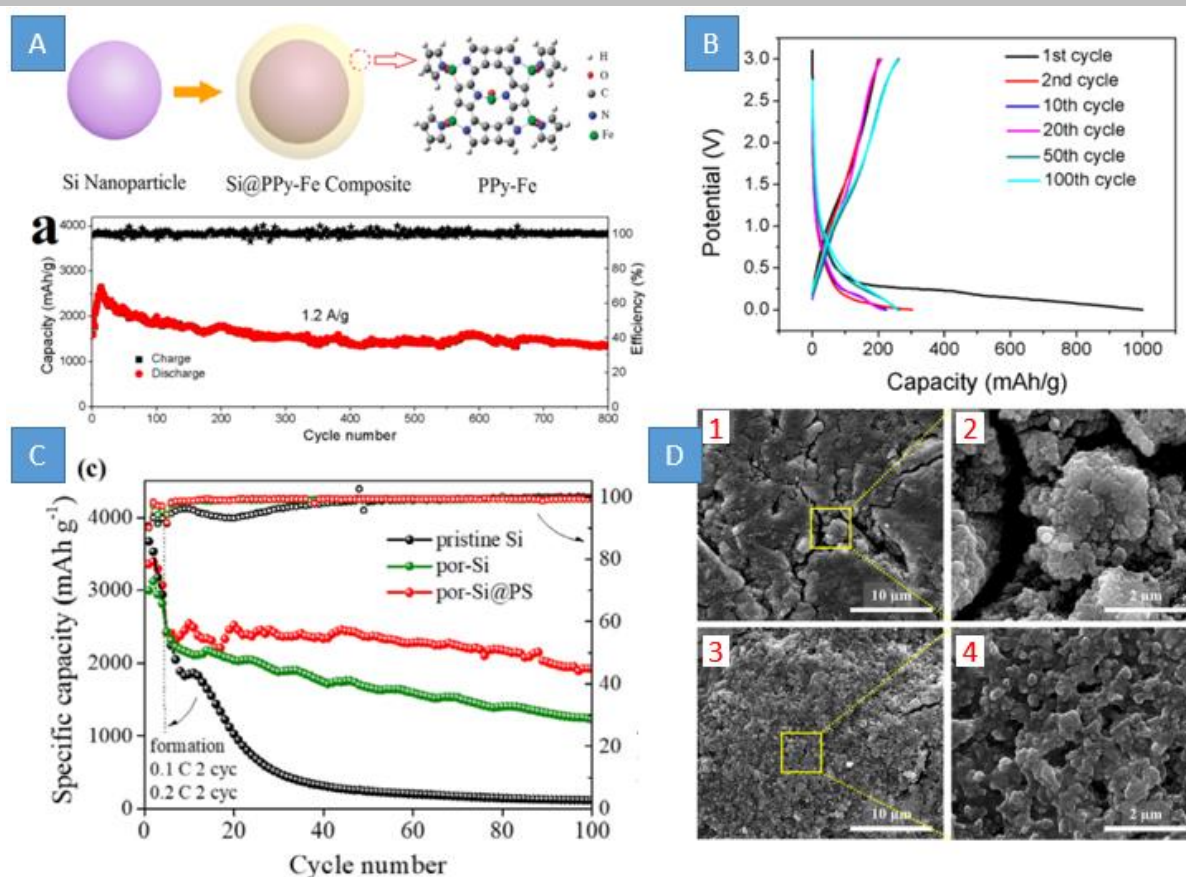
**Figure 5.** a) Schematic illustration of the synthesis process of Si@PANI-SPA core-shell and b) TEM image of the material produced with this method. c) Long term electrochemical cycling tests of Si nanoparticles, Si@PANI core-shell and Si@PANI-SPA core-shell at  $1.2 \text{ A.g}^{-1}$ . d) TEM picture of Si@/PPP structure. e) Electrochemical cycling tests of Si nanoparticles and Si@PPP core-shell at  $100 \text{ mA.g}^{-1}$  for 10 cycles and  $500 \text{ mA.g}^{-1}$  afterward. f) EIS spectra of a Si@PPP electrode at different cycles, with the equivalent circuit. Reproduced with permission Ref. [62] (a,b,c). Copyright 2016, Royal Society of Chemistry; ref. [63] (d,e,f). Copyright 2019, American Chemical society.

initial value after 20 cycles at low current ( $200 \text{ mA.g}^{-1}$ ). Here the effect of the dopant is even more impressive, as comparatively, without it and even with adding binder, no stability can be found. However, the material shows limitations, lacking stability at higher current ( $1.2 \text{ A.g}^{-1}$ ), and only besting the precursor in life expectancy (figure 5c). However, it is still a binderless and carbonless electrode so the active content is high and the electrode formulation is thus not optimized. The purposes of the dopant are explained to be activating the PANi, to have it contribute to electronic conduction and add adhesion between the core and the shell. This work also shows that an organic coating can be used as way more than a conformal coating. It can also be used to reduce the need of binder or even conductors. Another conductive polymer that can coat silicon is polyphenylene (PPP).<sup>[63]</sup> In their work, J. Zhang et al. used sand milling to first reduce the silicon particle size down to around 100 nm, and coated the newly created surfaces with PPP (Figure 5d). The exfoliated sheets of polymer react with active sites on the Si surface by  $\pi$ -stacking or with dangling bonds according to the authors. Due to the synthesis process, the material is constituted of irregular micro-aggregates of PPP-coated Si nanoparticles. The absence of PPP peaks in XRD indicates that the coating is amorphous. The electrochemical properties of the material are rather good, greatly improving both the stability and the coulombic efficiency (Figure 5e). Even though PPP is reacting with lithium (via a doping/de-doping mechanism), the authors explained improvements by the change of nature of the SEI created on PPP, and not on Si. Electrochemical impedance spectra, taken during the battery lifetime, show that the SEI is quickly stable, contrasting with bare-Si anodes (Figure 5f).<sup>[64]</sup> Another point to highlight out

of this study is the one-pot synthesis method in contrast with the usually rather hard and long processes for most organic shells.

In 2016, Zhou et al. made use of polypyrrole-Fe (PPy-Fe) organo-metallic coordination complexes to coat silicon nanoparticles.<sup>[65]</sup> The resulting layer helps with electronic conduction, providing pathways to the trapped Si core, but also shows a stable surface for the SEI growth. The synthesis method is simple and scalable, as it only requires the coordination complex. The resulting material shows impressive electrochemical performance when the layer thickness is optimized (figure 6a). The authors compare three synthesis loadings: 20, 50 and 66.7 wt%, showing that the ideal one would be 50 wt%. To our knowledge, this 50 wt% loading has one of the highest capacities after 50 cycles that has been reported in the literature, around  $3000 \text{ mAh.g}^{-1}$  at  $300 \text{ mA.g}^{-1}$ . They proposed that such performance can be related to a stable SEI layer and better conductivity, but it is also possible that the reaction of lithium with PPy-Fe adds some capacity (figure 6b). The other two have a lower capacity retention and a lower starting capacity, respectively, as well as what can be seen as a resistive behavior. Due to its coulombic efficiency of only 20 % for the first cycle, the electrochemically active PPy-Fe significantly contributes to the high initial irreversibility of the core-shells. This example shows that caution should be taken with active shells, as they have great impact on ICE. Overall, the core-shells synthesized by this group have interesting electrochemical performance even with high current density ( $1500 \text{ mAh.g}^{-1}$  after 800 cycles at  $1.2 \text{ A.g}^{-1}$ ). More recently, Tran et al. showed the possibilities of using an organic coating as a way to make Si microparticles relevant.<sup>[66]</sup> In their

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**Figure 6.** a) Schematic illustration of the synthesis process of Si@PPy-Fe core-shell and associated long term electrochemical cycling tests at 1.2 A.g<sup>-1</sup>. b) Voltage profiles of the 1<sup>st</sup>, 2<sup>nd</sup>, 10<sup>th</sup>, 20<sup>th</sup>, 50<sup>th</sup> and 100<sup>th</sup> cycles of PPy-Fe based electrode at 100 mA.g<sup>-1</sup>. c) Electrochemical cycling tests of Si, porous-Si and porous-Si@PS core-shell at 0.5 C (2 cycles at 0.1 C and 2 cycles at 0.2 C at the start). d) FE-SEM pictures of porous-Si (1,2) and porous-Si@PS (3,4) after 100 cycles. Reproduced with permission Ref. [65] (a,b). Copyright 2016, American Chemical Society; ref. [66] (c,d). Copyright 2020, Elsevier.

research, they first produced their own porous silicon, porous-Si, by chemically etching a commercial Si micro powder (around 5  $\mu\text{m}$ ) assisted with silver. They obtained a porous silicon with a five-time higher surface area than that of the commercial precursor. By thermolytic grafting, they then coated the porous particles with a layer of polystyrene (PS), proved to be around 5 nm thick by HR-TEM. It is important to note that they treated their material with HF after every step to ensure the absence of any silicon oxide. It is obvious from this article that PS is degraded into carbon, but the difference with a simple carbon coating is the existence of Si-C bonds as well as the styrenic fragments that are left. Both the porous silicon and the coated porous silicon have relatively good stable and high reversible capacities. However, the low carbon content of under 1 wt% has tremendous effects on the electrochemical properties (figure 6c). After an initial capacity loss of around 40% for the first 5 cycles, the porous-Si@PS has an 80% reversible capacity until the 100<sup>th</sup> cycle. As proposed by the authors, three phenomena can explain those results. Firstly, the grafted Si-C species help alleviate the strain caused by the volumetric expansion, as shown by SEM on the cycled electrodes (figure 6d). The coated material has a well-maintained disposition, contrasting greatly with the cracks that are mostly seen on Si-based electrodes. Secondly, the coating prevents the electrolyte degradation, providing a more stable SEI by being at the interface. Finally, the porosity of Si and the carbonaceous layer provide better ionic diffusion and electronic conductivity, respectively, and

rate recovery, as shown by the C-rate experiments and EIS measurements. One additional interesting point is the comparison of two synthesis temperatures. The authors indeed show that using a higher temperature degrades the PS, thus reducing the improvements obtained for electrochemical performance.

Whereas carbon and inorganic coatings have been studied for quite a while, organic coatings are rather new to the field of Si based core-shell structures. However, they have shown great promises, opening the field to new possibilities. In fact, those few examples suggest that trying to constrict the expansion of silicon might not be the way to go. We have seen previously that “hard” coating has a lot of trouble finding stability, gradually losing capacity over time because of the shell gradually failing. Here, organic coating accommodates the expansion with little to no breakage of the interface and/or the electrode film. Some questions marks are still left. For example, as said previously, most syntheses require long, hard and expensive processes that would be difficult to scale-up. In addition, ICE is low, as the reactivity of lithium toward polymers is high. We have shown in sections 2-4 that carbon, inorganic and organic coatings can improve greatly the performances of Si electrodes. However, each type of shell has its own strengths and weaknesses, thus, combining at least two of them could create synergetic effects, reducing the drawbacks of those coatings.

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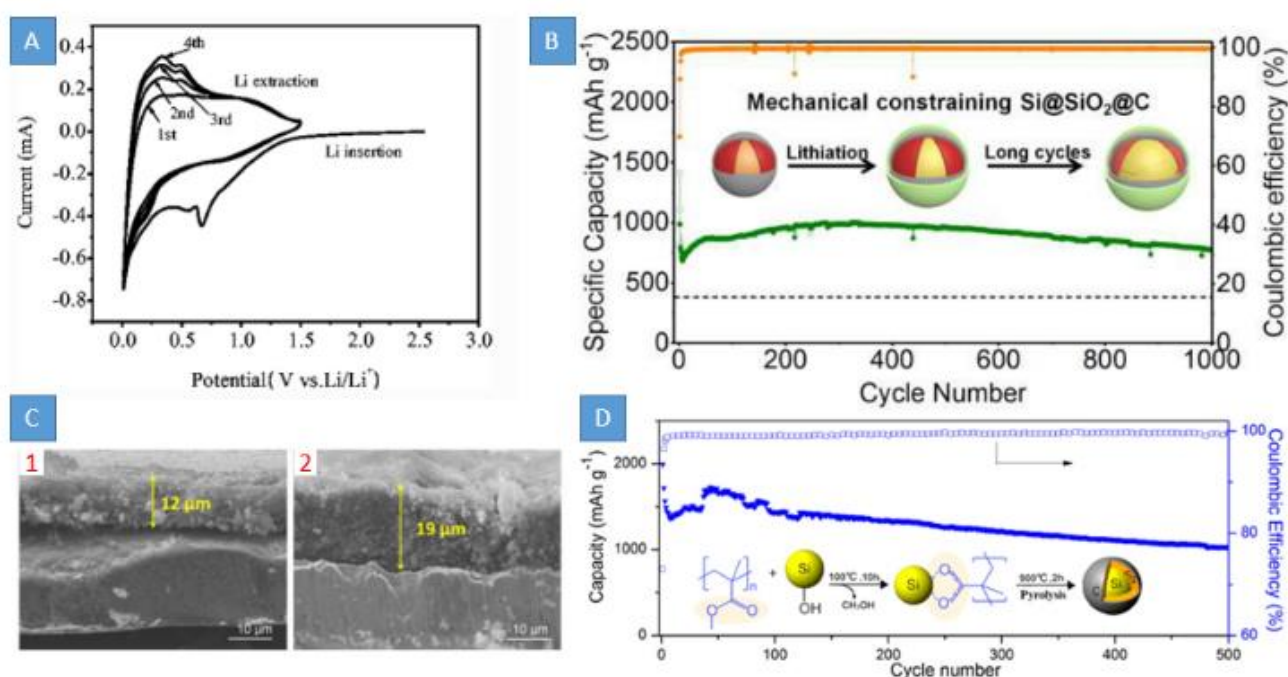
## 5. Double-layer coatings

Multi-coated silicon particles should be considered to combine the advantages of different types of coatings as described above while reducing their weaknesses. Even if it often renders the synthesis more tedious, some have found ways to fabricate such structures without many efforts and such works are discussed in this section. Multiple arrangements and strategies are possible: a constraining first shell and another one to enhance ionic and electronic conductivities, a constraining coating over a soft shell to better alleviate the expansion while keeping the SEI stable or even double hard shells.

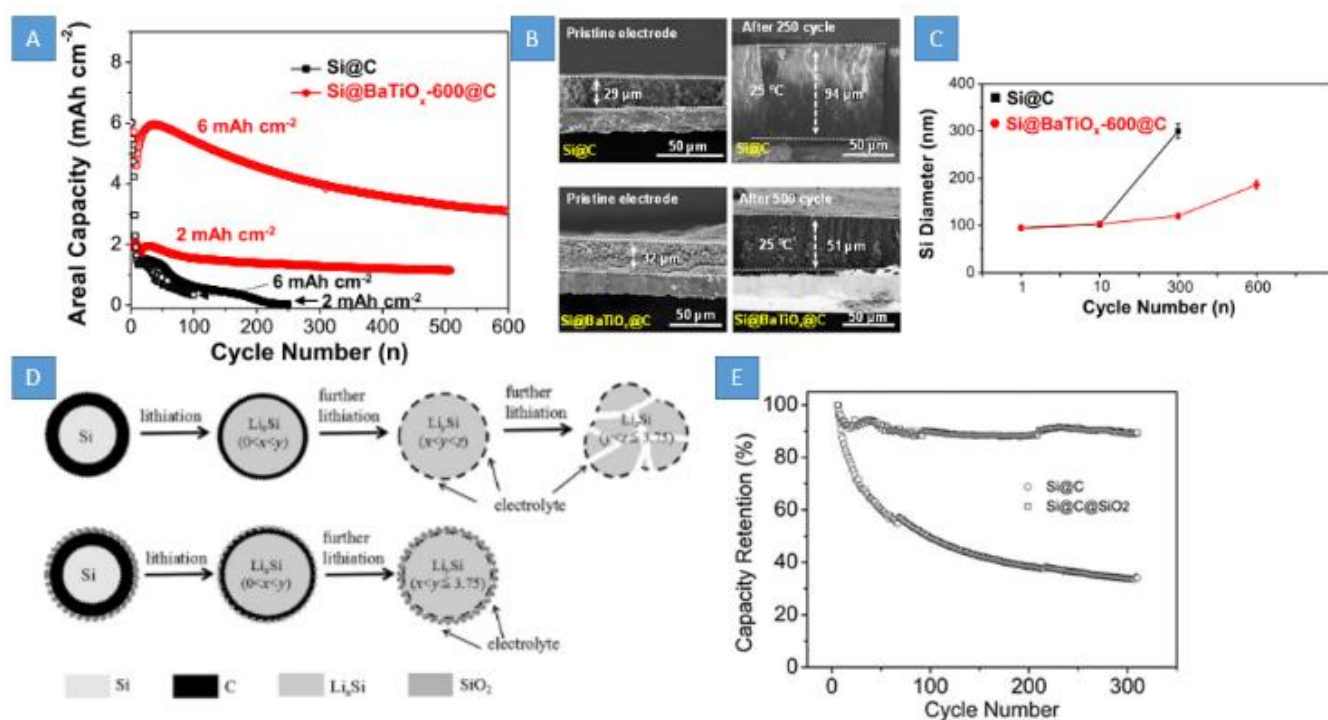
If  $\text{SiO}_2$  and carbon have been studied thoroughly as coating individually, the combination of both has also been a subject closely looked at. As first example of hard-soft double-shell,  $\text{Si}@\text{SiO}_2@\text{C}$  was synthesized by Tao et al.<sup>[67]</sup> The silica layer was obtained by simply annealing silicon in a furnace under air; the carbon was added thanks to epoxy resin carbonization afterward. The high carbon content, close to 60 wt%, and the use of epoxy jellification process put this material closer to a composite. The stability is correct, superior to  $845 \text{ mAh.g}^{-1}$  during 80 cycles, but the irreversibility of the first cycle is high, at 49%. It was attributed to a high-SEI formation over the amorphous carbon layer characterized by Raman spectroscopy ( $I_d/I_g \sim 1.26$ ) and the lithiation of the silica layer, forming  $\text{Li}_4\text{SiO}_4$  irreversibly as observed by cyclic voltammetry (figure 7a). The layer of  $\text{SiO}_2$  is quite thick, measuring 5 nm around the 100-200 nm silicon particles, and disordered as shown by the existence of only one broad XRD peak. It was also shown that even the formation of

$\text{SiO}_x$  layer benefits to the electrochemical performance often explained by having the formation of this extra layer of conductive lithium-silicon oxide.<sup>[32,68,69]</sup> Later, Zhang et al. developed core-shell nanoparticles where the formation of the silica layer was controlled.<sup>[70]</sup> Whereas the  $\text{SiO}_2$  layer in the previous examples was simply obtained by oxidation of the particles, in the latter work the  $\text{SiO}_2$  coating was made by hydrolysis of tetraethyl orthosilicate (TEOS). The carbon layer was then added by self-polymerization of dopamine, as seen in the work of Q. Ma et al.<sup>[34]</sup> The BET curves show that the first coating of crystalline silica helps reduce a lot the overall porosity, which is detrimental for carbon layers as it leads to a huge irreversibility on the first cycle. It is related to the surface groups of silica that regulate the polymerization and bonding of dopamine. The  $\text{SiO}_2$  uniform layer constrains the growth of Si during cycling, by mechanical pressure but also by reducing the  $\text{Li}^+$  ion diffusion. The capacity retention of the final core-shells is better than with only the carbon, by far. At  $1 \text{ A.g}^{-1}$ , the material retains 50% of its initial capacity after 1000 cycles, but with a low ICE of around 70% and high capacity loss on the first cycles (figure 7b). The high initial irreversibility can be explained by the formation of the SEI and  $\text{Li}_4\text{SiO}_4$ . The latter is believed to have a respectable ionic conductivity, and is also responsible for constraining silicon in this case.<sup>[71]</sup> In fact, one impressive point is that the film only expands to 151% of its original thickness, which is lower than most silicon based electrodes, moreover at this high percentage of silicon content, here around 65 wt% in the film (figure 7c).<sup>[72-74]</sup> Jiang et al. obtained similar performances (figure 7d).<sup>[68]</sup>

Park et al. made use of  $\text{BaTiO}_x$  as first layer, hoping to stabilize the SEI and “clamp” the Si particles to avoid degradation.<sup>[75]</sup> The



**Figure 7.** a) Cyclic voltammetry of  $\text{Si}@\text{SiO}_2@\text{C}$  double core-shell at  $0.5 \text{ mV.s}^{-1}$  between 0.01 V and 1.5 V. b) Schematic representation of  $\text{Si}@\text{SiO}_2@\text{C}$  core-shell and associated electrochemical cyclic test at  $1 \text{ A.g}^{-1}$ . c) Cross section SEM of  $\text{Si}@\text{SiO}_2@\text{C}$  electrodes before cycling (1) and after 1000 cycles (2). d) Schematic representation of  $\text{Si}@\text{SiO}_2@\text{C}$  core-shell produced by one step synthesis and associated electrochemical cycling test at  $1 \text{ A.g}^{-1}$  (After a first cycle at  $100 \text{ mA.g}^{-1}$  and a second at  $500 \text{ mA.g}^{-1}$ ). Reproduced with permission Ref. [67] (a). Copyright 2014, Springer; ref. [70] (b,c). Copyright 2020, Elsevier; ref. [62] (d). Copyright 2016, American Chemical Society.

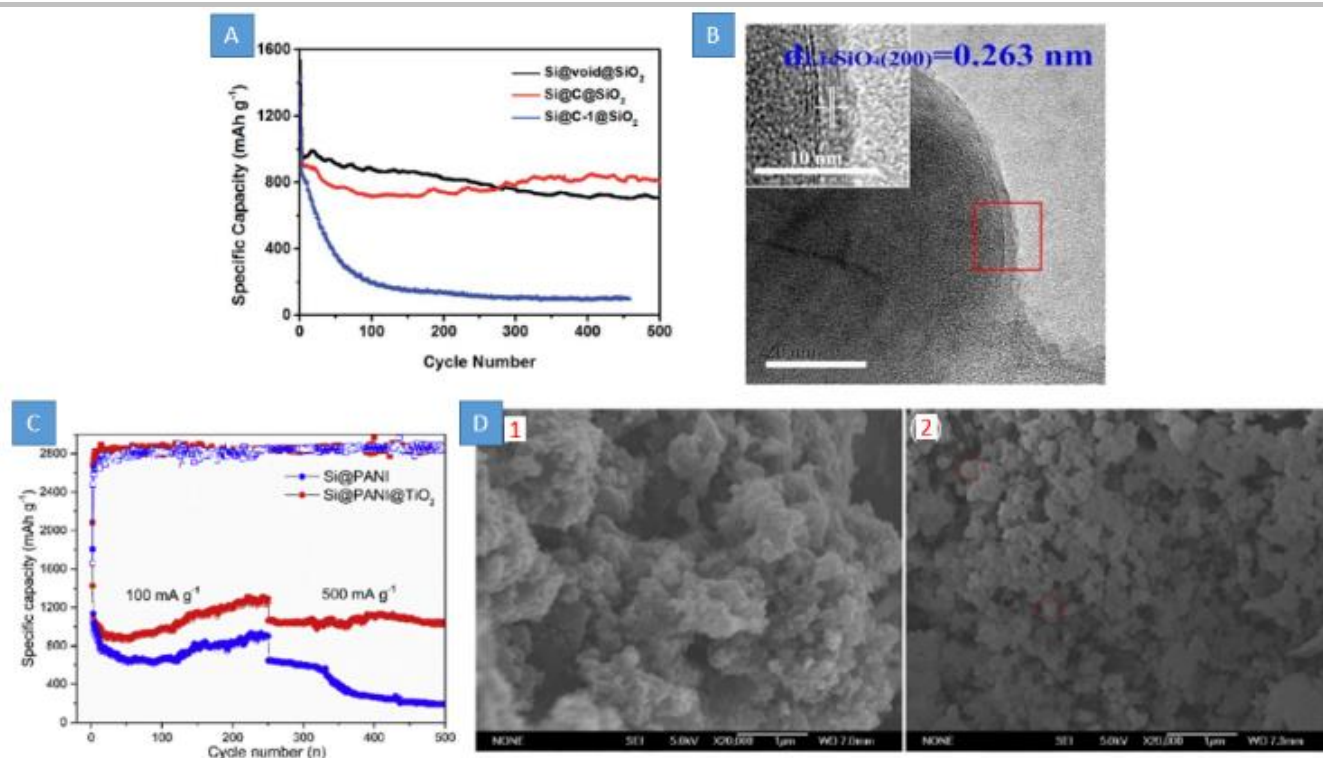


**Figure 8.** a) Cycling performance of Si@C and Si@BaTiO<sub>x</sub>@C core-shells at 1C for different aerial capacities. b) SEM thickness study of the two previous core-shells: pristine and after cycling. c) Variations of the silicon particle diameter as a function of cycle number for Si@C and Si@BaTiO<sub>x</sub>@C core-shells. d) Schematic representation of the behavior during lithiation of Si@C and Si@C@SiO<sub>2</sub> core-shells. e) Associated capacity retention curves during electrochemical cycling tests at 200 mA.g<sup>-1</sup> (after 5 cycles at 50 mA.g<sup>-1</sup>). Reproduced with permission Ref. [75] (a,b,c). Copyright 2016, Elsevier; ref. [76] (d,e). Copyright 2017, Wiley.

second layer is made of carbon to help with conductivity. After a sol-gel synthesis for the barium titanate, an extra carbon layer was added by chemical vapor deposition (CVD), using toluene as precursor. The resulting core-double-shell particles are composed of 83 wt% of silicon, 10 wt% of BaTiO<sub>x</sub> and 7 wt% of carbon, which is said to be optimized in order for the layers to stay mechanically stable in this case. It is of importance to note that there was no silica layer around the Si precursor as it was chemically removed. The stability of the capacity on cycling is impressive, even at high aerial capacity (figure 8a). Long-term cycling abilities are always kept at higher temperature, here 60°C. The overall capacity retention and stability are shown to be due to the mechanical and chemical stability of the compound. SEM and TEM pictures (figure 8b) show that even after 500 cycles, the coating is still in place and hinders the expansion greatly compared to a simple carbon coating (figure 8c). The change of nature of the SEI was also studied with XPS, where it was deduced that a more stable and thinner SEI was growing onto the double core-shell.

Yang et al. worked on the same shell materials, C and SiO<sub>2</sub>, but inverting the layers to obtain soft-hard double layer.<sup>[76]</sup> They theorized that carbon would work as a buffer, and that the SiO<sub>2</sub> surface, or more the Li<sub>4</sub>SiO<sub>4</sub> formed during the first lithiation, provides a stable surface for the SEI. A rough idea is provided in figure 8d. The existence of an amorphous SiO<sub>2</sub> shell was proven by XPS, TEM and XRD, while cyclic voltammetry shows the lithiation of this shell at the first cycle. The cycling stability is great, retaining 90% of the initial capacity after 300 cycles (figure 8e).

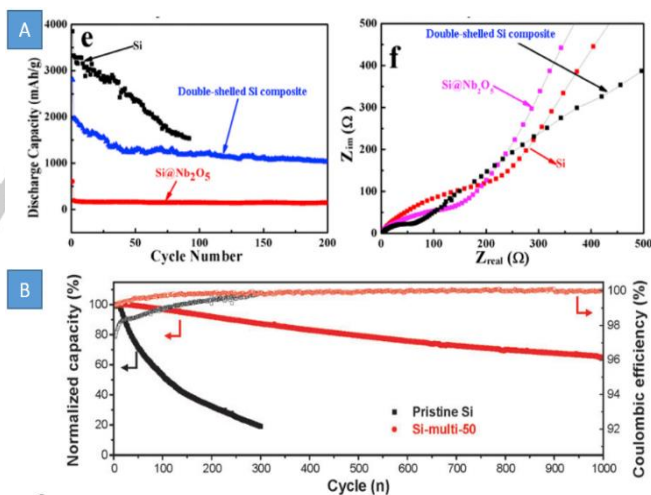
However, the low silicon content, expected to be about 30% based on the starting capacity of 1205 mAh.g<sup>-1</sup>, also helps improve greatly the stability. Here the order of the layers is said to be relevant, as carbon helps cushion the expansion, while silica has the mechanical strength to keep the coating from decaying. Wu et al. obtained similar results, with a different synthesis method, validating the structure and even showing that the long-term stability could even be better than a yolk-shell material (figure 9a).<sup>[77]</sup> Ai's work went a step further, by forming Li<sub>4</sub>SiO<sub>4</sub> by heat treatment rather than electrochemically.<sup>[78]</sup> They showed by Raman spectroscopy and XRD the existence of graphene and lithium silicate, respectively, while HR-TEM displays the double shell structure. The low content of graphene in the first layer (8 wt%) could explain the high capacity losses on the few first cycles, as carbon is not acting as buffer but only as conductive component. This work however shows that it is possible to improve the ICE, by removing the capacity loss due to SiO<sub>2</sub> lithiation. Post-mortem TEM reveals also that the particles keep their mechanical integrity after 200 cycles thanks to the coating, which could explain the observed good capacity retention (figure 9b). As another example of soft-hard double-shell, Gu et al. made use of the flexibility and conductive properties of PANi, allied to the toughness of TiO<sub>2</sub>.<sup>[79]</sup> Similarly to previous works, they hypothesized that the elasticity of PANi would help to absorb volume expansion of the Si core during cycling, while TiO<sub>2</sub> provides a rather rigid shell for the SEI stability as observed by EIS and SEM. The synthesis of such structure is relatively easy, as it relies on PANi *in situ* growth followed by tetrabutyl titanate hydrolysis. The obtained material shows a uniform coating of 30 nm of PANi and 20 nm of TiO<sub>2</sub> over the 80 nm silicon particles.



**Figure 9.** a) Long term electrochemical cycling tests of two Si@C@SiO<sub>2</sub> core-shells with different carbon contents and a Si@void@SiO<sub>2</sub> yolk-shell at 100 mA.g<sup>-1</sup>. b) TEM picture of a Si@C@Li<sub>4</sub>SiO<sub>4</sub> particle after the 200<sup>th</sup> cycle. c) Long term electrochemical cycling tests for Si@PANI and Si@PANI@TiO<sub>2</sub> at 100 mA.g<sup>-1</sup> (250 cycles) and 500 mA.g<sup>-1</sup> afterward. d) SEM images of Si@PANI (1) and Si@PANI@TiO<sub>2</sub> after 500 cycles. Reproduced with permission from ref. [77] (a). Copyright 2018, Royal Society of Chemistry; ref. [78] (b). Copyright 2018, Elsevier; ref. [79] (c,d). Copyright 2018, Elsevier;

The electrochemical properties that result are a relative stability over 500 cycles, with high-rate capability and reversibility (figure 9c). The initial capacity fade is again quite high but is recovered along time at low currents. The improvement over PANi is clear showing the synergy effect of organic and inorganic double shell. Nevertheless, as shown above, TiO<sub>2</sub> does not show the best performance for inorganic materials, so there may be room for further improvements. But once again the oxide coating showed direct effect, as electrode aspect is better kept after 500 cycles (figure 9d).

Finally, double hard shells were also considered to constrain Si core volume expansion and obtain a stable SEI. Double oxide layer structures have attracted attention too, relying on a silicate layer similar to the ones shown before. Du et al. synthesized, by co-precipitation and calcination, double core-shell structures comprised of a first Li<sub>2</sub>SiO<sub>3</sub> layer and an Nb<sub>2</sub>O<sub>5</sub> outer shell.<sup>[80]</sup> Compared to Si@Nb<sub>2</sub>O<sub>5</sub> nanoparticles, where the interface was not lithiated, better electrochemical results were obtained (figure 10a). The authors attribute the capacity losses in non-lithiated Si@Nb<sub>2</sub>O<sub>5</sub> particles to a thick SiO<sub>2</sub> layer, severely hindering the Li<sup>+</sup> ion diffusion (figure 10a). The capacity of Si@Li<sub>2</sub>SiO<sub>3</sub>@Nb<sub>2</sub>O<sub>5</sub> is decreasing over the cell-life, never really attaining stability. Nonetheless, the improvements over bare-Si are obvious, and the rate cyclability is also good. Those improvements are linked to the decrease of impedance brought by the lithium silicate layer and the accommodation of the volumetric expansion by the second layer, Nb<sub>2</sub>O<sub>5</sub>. Lee et al. used a similar synthesis approach, this time producing



**Figure 10.** a) Long term electrochemical cycling tests of Si nanoparticles, Si@Nb<sub>2</sub>O<sub>5</sub> and Si@Li<sub>2</sub>SiO<sub>3</sub>@Nb<sub>2</sub>O<sub>5</sub> core-shells at 200 mA.g<sup>-1</sup> (left) and associated EIS spectra (right). b) Long term cycling properties of Si nanoparticles and Si@Li<sub>4</sub>SiO<sub>4</sub>@LTO core-shell at 1C. Reproduced with permission Ref. [80] (a). Copyright 2018, Elsevier; ref. [81] (b). Copyright 2015, Royal Society of Chemistry.

Si@Li<sub>2</sub>SiO<sub>3</sub>@LTO particles.<sup>[81]</sup> They showed really good capacity retention, with 65% of the initial capacity left after 1000 cycles (figure 10b). And while the specific capacity is lower than other Si based core-shell particles (around 800 mAh.g<sup>-1</sup> after 100 cycles)

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it is still twice the one of carbonaceous anodes, while also possessing good rate capabilities associated to oxide coatings. The authors show by XPS, EIS and galvanostatic intermittent titration technique (GITT) that their double coating decreases the decomposition of the electrolyte and keeps a stable SEI, while enhancing the electronic and ionic conductivities. It also helps maintaining the structure of the particles.

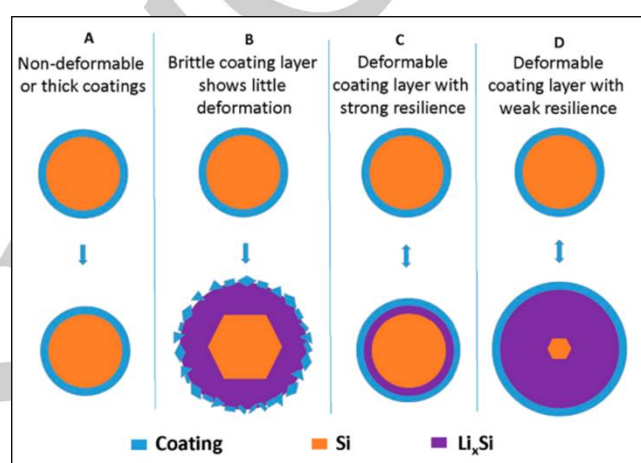
It is difficult at this time to conclude on double-layer coated silicon particles such as those presented in this section. In fact, as there is a higher proportion of non-active material the effects of double-layer coatings are harder to decipher. In addition, while some materials showed the same limitations as their individual constituents, some had definite synergetic benefits coming from their double layers. The wider array of possibilities makes it near impossible to generate a perfect candidate. Nevertheless, adding a carbon layer seems to improve nearly every time a previous core-shell. Another important thing to deduce from this part is that the oxide layer often created during the synthesis of a coating is not to be forgotten. It has a crucial impact on the electrochemical performance of silicon particles if not managed adequately. Some of the examples presented in this section have shown to be the closest to a truly useable anode, with low ICE and adequate capacity retention, while maintaining high capacity. This opens attractive perspectives for the application of the synergetic effects in double-shell coated Si nanoparticles.

## 6. Conclusion

The general trends that take shape from the different examples reviewed in this mini-review are summarized on Figure 11.<sup>[82]</sup> Carbon coatings help effectively alleviate the volume expansion and the resulting phenomena associated. Their properties also reduce the resistivity of the electrode and provide a more stable surface during the lifetime for the SEI growth. However, carbon coatings suffer from high irreversibility in the first cycles, due to the SEI formation on the often-porous carbon. The loss on those first cycles is detrimental to the use of such Si@C core-shells, as the ICE hardly attains 80 %. The stability is never really reached, the electrode losing capacity at every cycle, even if it is not much, which is mostly due to the coating being not elastic or resistant enough.

Inorganic coating improvements are more heterogeneous. Pure metal coatings improve electronic conductivity, but the coating is often too brittle to hold, needing pathways to conduct ions. Oxides have shown good results, being good ionic conductors and constraining the volumetric expansion, keeping the particles and SEI intact. If electrodes with long-term stability can be obtained, with coatings such as  $\text{LiAlO}_2$  or  $\text{TiN}$ , the first irreversible capacity makes them unreliable, losing around 33% of the starting capacity in both cases. Organic layers, even though stemming from relatively recent studies, have already shown great promises. While some provide results similar to carbon or inorganic coating (low ICE, rapid loss then slow decrease other time), some polymers showed long term stability, acceptable ICE and that, even on micron-sized silicon. That type of coating can

also be used in binder-less electrodes, or even additive less. Their flexibility can accommodate the expansion while keeping the electrolyte away from the core. However, the complex synthesis methods and low conductivity are still a problem, and the works reported here are far from commercial applications though. Finally, the use of a double-layer coating has been showed as an interesting structure. While it seems difficult to synergize the layers, some authors proved it could be achieved. Adding a carbon coating other a pre-existing core-shell is efficient, as it helps said core-shell to keep electrical contact with the system. Combining a strong outer shell with a softer inside shell can provide relief against stress, while keeping a stable surface for the SEI to grow and improves both conductivities. Thus, dual-layer materials, with synergetic layer properties, might be the closest to the requirements of industrial and commercial electrodes.



**Figure 11.** Illustration of the different behaviors of core-shell structures in relation to the nature of the layer. Reproduced with permission from ref. [82] Copyright 2015, American Chemical Society.

Optimization of core-shell design is required for commercial applications and several trails can be followed. The particle size optimization will always bring steady improvements, as shown in figure 8c, as the core-shell structures possess critical sizes where the coating will or will not break. Focus has to be put however, on design where the ICE is low, because it is mostly due to the nature of the shell and not its dimensions. Organic coating are rather new but have shown promises, if the synthesis can be simplified and upscaled, they will have a great outlook. Double coatings are the most elaborate and since synergetic couples have been found, we think that some optimization can bring them up to the expectation of industry. The electrode formulation has to be studied also. Interactions between the external shell and the binder are different than with Si, but in most works, the basic binders for uncoated silicon based anodes were used. The SEI too will change in composition and properties, but once again most of the time the electrolytes assessed were ones optimized for bare silicon. In addition, developing self-healing or durable bonds between the components of the electrode is important to help keep its integrity in the long run. As such, functionalized coating or coating capable of creating secondary networks should be studied. However, using a precursor such as  $\text{SiO}_x$  or Si microparticles would be a more commercially oriented move and multiple works have already shown promising results following the

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principles introduced.<sup>[83,84]</sup> The precursors are of micrometric sizes and the innovative electrode composition/formulation is plainly taken into account from the start.

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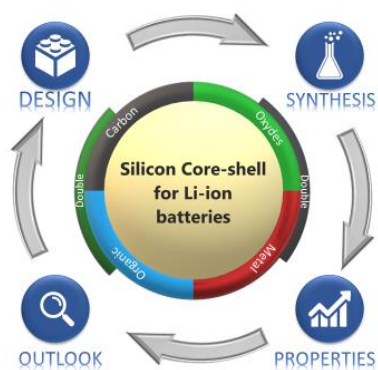
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**Entry for the Table of Contents**

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The core-shell architecture has been recognized as one of the most promising solutions to enable higher silicon content in Li-ion anodes. In this mini-review, we report different types of coatings on silicon particles including carbon, inorganic, organic and double-layer shells from some selected examples. The synthesis methods, structure characterization, main properties and resulting electrochemical performance are outlined. Improvements over silicon are decrypted and trends for future works are objectively identified.