# Silicon-Based Self-Assemblies for High Volumetric Capacity Li-Ion Batteries via Effective Stress-Management

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This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the <u>Version of Record</u>. Please cite this article as <u>doi:</u> 10.1002/adfm.202002980.

# Abstract

Silicon nanoparticles (Si NPs) have been considered as promising anode materials for next-generation lithium-ion batteries, but the practical issues such as mechanical structure instability, low volumetric energy density limit its development. At present, the functional energy-storing architectures based on Si NPs building blocks have been proposed to solve the adverse effects of nanostructures, but how to design ideal functional architectures with excellent electrochemical performance is still a significant challenge. This study shows that the effective stress evolution management is applied for self-assembled functional architectures via cross-scale simulation and the simulated stress evolution can be as a guide to design a scalable self-assembled hierarchical Si@TiO<sub>2</sub>@C (SA-SiTC) based on core-shell Si@TiO<sub>2</sub> nanoscale building blocks. It is found that the carbon filler and TiO<sub>2</sub> layer can effectively reduce the risk of cracking during (de)lithiation, ensuring the stability of the mechanical structure of SA-SiTC. The SA-SiTC electrode shows long cycling stability (842.6 mAh g<sup>-1</sup> after 1000 cycles at 2 A g<sup>-1</sup>), and high volumetric capacity (174 mAh cm<sup>-3</sup>), high initial Coulombic efficiency (80.9%) and stable solid-electrolyte interphase (SEI) layer. This work provides insight into the development of the structural stable Si-based anodes with long-cycle-life and high volumetric energy density for practical energy applications.

The effective stress evolution management is applied for self-assembled functional architectures via cross-scale simulation and the simulated stress evolution can be as a guide to design a scalable self-assembled hierarchical Si@TiO<sub>2</sub>@C (SA-SiTC)

based on core-shell Si@TiO<sub>2</sub> nanoscale building blocks. This work provides insight into the development of the structural stable Si-based anodes with long-cycle-life and high volumetric energy density for practical energy applications.

# Keywords

stress-management, self-assembled hierarchical architecture, Si@TiO<sub>2</sub> building blocks, high volumetric capacity, Li-ion batteries

### 1. Introduction

Lithium-ion batteries (LIBs) with high energy density and high bulk density are critical to the development of consumer electronics.<sup>[1]</sup> Alloy-type anodes (Si, Ge, Sn, Sb, etc.) have higher energy densities than graphite that currently used in LIBs.<sup>[2]</sup> Among them, the silicon (Si) anode is attracting attention due to the large theoretical capacity of ~ 4200 mAh g<sup>-1</sup> (actual specific capacity ~ 3759 mAh g<sup>-1</sup>), a low redox potential (~ 0.4 V *vs*. Li/Li<sup>+</sup>), non-toxic and productive reserves.<sup>[3]</sup> However, the main challenges for Si anodes are a massive volume change (~ 280%) during (de)lithiation, the formation of electrochemical lithiation at the boundary between lithium-rich Li<sub>x</sub>Si and Si phases causes increase stress on the outer surface of the Si particles, which causes severe surface cracking.<sup>[4]</sup> The structural instability, induced by pulverization, has been considered to be one of the main causes of rapid capacity fading in Si-based electrodes, which hinders the application of Si-based anode in LIBs.<sup>[5]</sup>

To alleviate the adverse mechanical effects, recently, considerable efforts have been made to explore Si-based anode materials that exhibit integrated advantages, in the hope of circumventing the problems synergistically for enhanced performance. A variety of different shapes and methods <sup>[6]</sup> such as nanoparticles, <sup>[7]</sup> porous structures, <sup>[8]</sup> additives, <sup>[9]</sup> alloy composites, <sup>[10]</sup> carbon coating layer, <sup>[11]</sup> and novel binders <sup>[12]</sup> have been employed for the preparation of Si-based materials as LIBs anodes. TiO<sub>2</sub> (amorphous, anatase) has received significant attention as a conductive coating for Si NPs owing to fast Li<sup>+</sup> insertion / extraction rate, negligible volume expansion (< 4%) during lithiation and effectively control the formation of SEI films.<sup>[13]</sup> Among them, amorphous TiO<sub>2</sub> coating renders an elastic behavior during (de)lithiation <sup>[14]</sup> and the anatase TiO<sub>2</sub> shell shows 5 times greater strength than the amorphous carbon shell, <sup>[15]</sup> both can be used to maintain Si NPs structural integrity, furthermore, preparation of an anode material with Si@TiO2@C core-shell structure to achieve excellent electrochemical performance.<sup>[16]</sup> However, it remains a considerable challenge that the reported conventional core-shell nanomaterials that cannot ensure long-cycle-life and high volumetric energy density due to the limit of low tap density or the structural instability (generally, the volume capacity (mAh  $cm^{-3}$ ) = gravimetric capacity  $(mAh \cdot g^{-1}) \times tap density (g \cdot cm^{-3})).$ <sup>[17]</sup>

To solve this problem, the mechanical pressing and intelligent self-assembly, which based on Si-based functional nanoscale building blocks, are employed to improve the tap density and structural stability of electrodes. <sup>[18]</sup> For instance, Cui *et al.* <sup>[19]</sup>

proposed a pomegranate-like Si/C microsphere, which had a high tap density and reserved enough room for expansion/contraction following (de)lithiation. But a preserved hollow space may be destroyed under a tight calendering process.<sup>[15]</sup> It is no doubt that maintaining the integrity of structures is essential for excellent electrochemical performance, and effective mastering stress evolution is critical to the integrity of electrode materials during the (de)lithiation.<sup>[20]</sup> It has been proved that the outer surface of the silicon particles has the largest tensile stress during the lithiation, <sup>[21]</sup> and the stress can be controlled by preparing different coatings to maintain the mechanical structure stability.<sup>[22]</sup> However, the stress of self-assembles electrodes belonging to multiple particles system, unlike the stress evolution of a single particle system, will be much affected by the interaction between assembled Si particles. Therefore, it is significant to consider the stress evolution between multiple particles system during (de)lithiation to achieve ideal functional architectures more accurately with high volumetric energy density and mechanical structure stability.

Herein, we developed a finite element model to simulate the stress evolution of self-assembled functional architectures, and use the effective stress-management model as a guide to design a scalable self-assembled hierarchical Si@TiO<sub>2</sub>@C (SA-SiTC) based on core-shell Si@TiO<sub>2</sub> nanoscale building blocks. Theoretical simulation combined with systematic experiments demonstrates that the carbon filler and TiO<sub>2</sub> layer can effectively reduce the surface tensile stress of Si NPs, reduce the

risk of cracking during (de)lithiation, and make SA-SiTC electrodes have optimized  $Li^+$  and electron transport paths. This design has the following four advantages: (i) primary particles use ~ 70 nm silicon to prevent the crack <sup>[24]</sup>; (ii) the TiO<sub>2</sub> layer and carbon provide the buffering effect, and the surface tensile stress of the Si is effectively reduced by the interaction between the particles in the unique self-assembled hierarchical architecture, which ensures the mechanical structure stability; (iii) the filled carbon skeleton and the surface-coated carbon layer not only provide fast diffusion path of electron, but also effectively limits the overgrowth of SEI film on the surface of SA-SiTC microspheres, which increases CE and improves cycle stability; (iv) the prepared self-assembled structure with high tap density significantly increases the volumetric capacity of the electrode. As a result, SA-SiTC exhibited a high volumetric capacity ( $\sim 1174 \text{ mAh cm}^{-3}$ ) with high initial Coulombic efficiency (80.9%), and stable solid-electrolyte interphase (SEI) layer, maintained morphological integrity during (de)lithiation. More importantly, the mechanic simulations, as effective stress-management model, showed that the outward tensile stress of the Si in the SA-SiTC is  $\sim 0.51$  times that of SiTC-NPs, and the specific capacity of SA-SiTC is ~ 2.33 times that of SiTC-NPs after 500 cycles. Besides, two types of full-cells based on the SA-SiTC anodes and commercial cathodes, including LiCoO<sub>2</sub> (LCO) and LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) were assembled and exhibited a high-energy density of 394.8 Wh kg<sup>-1</sup> and 362.6 Wh kg<sup>-1</sup>, 86% and 77.5% capacity retention for over 100 cycles, respectively, suggesting superior electrochemical

properties in a full-cell operation. This work provides insight into the development of the structural stable Si-based anodes with long-cycle-life and high volumetric energy density for practical energy applications.

# 2. Results and Discussion

Mechanical pressing or smart assembly is usually used to prepare the functional architectures with high tap density, but these architectures inevitably weaken the cyclic stability due to the interaction of Si expansion, as shown in Figure 1a. The contact between the particles is point-point contact, and the stress concentration near the point-point contact causes excessive stress gradient due to the Si expansion during lithiation, which can easily cause the particle to crack. To avoid the stress concentration of particles, we propose a progressive stress management strategy. This strategy is mainly achieved by changing the contact mode of the particles and increasing the surface contact of the particles by filling the gaps between the Si particles. During the expansion process, the surface of the particles is subjected to uniform compressive stress by mutual extrusion of the filler, which reduces the crack problem caused by stress concentration. Among them, the filler should have dual diffusion path performance of Li<sup>+</sup> and electrons. On this basis, it is proposed to cover the Si surface with a shell layer to further make the stress on the Si surface more uniform. The shell layer and the filler should serve as a stress management interlayer during the lithiation, which is applied on the Si surfaces in a reverse and progressive

manner by buffering the expansion force. To verify the correctness of the theory, we perform a combination of theoretical simulations and experiments; among them, the shell layer is set as a  $TiO_2$  layer, and the filler is set as carbon.

We design a new chemomechanical model to calculate the generation and distribution of mechanical stress during lithiation. In this model, an elastic-perfectly plastic constitutive model and a nonlinear diffusion model are used to the mechanical response of the lithiated Si. The yield stress and the elastic modulus of Si are set to depend nonlinearly on the Li<sup>+</sup> concentration. Specifically, we take a non-linear function Equation 1 to introduce the direct relationship between Si and Li<sup>+</sup>

$$D = D_0 \left[ 1 / (1 - c) - 2\Omega_c \right]$$
 (1)

Wherein  $D_0$  is the diffusion constant, c is the normalized Li<sup>+</sup> concentration, which is controlled by the standard diffusion equation.  $\Omega_c$  is the activation volume of Li<sup>+</sup> diffusion, and the concentration curve near the reaction front is controlled by adjusting  $\Omega$ . The elastic-perfectly plastic constitutive model is used to simulate morphological change and stress generation.

The total strain rates

$$\varepsilon_{ij} = \varepsilon_{ij}^{c} + \varepsilon_{ij}^{e} + \varepsilon_{ij}^{p}$$
<sup>(2)</sup>

Where e is the elastic strain rate and elastic behavior obeys Hooke's law; p represents the plastic strain rate and complies with the J2-flow rule; c represents the chemical strain rate caused by lithiation

$$\varepsilon_{ii}^{c} = \beta_{ii}$$

Where  $\beta_{ij}$  is the lithiation expansion coefficient;  $\dot{c}$  is the value according to the lithiation state. Hoop stress can be expressed as:

$$\sigma_{c}(r) = \frac{1}{3}(\sigma_{x} + \sigma_{y} + \sigma_{z}) = \frac{2\Omega E}{9(1-v)} [\frac{3}{R^{3} - r^{3}} \int_{0}^{R} C(r)r^{2}dr - C(r)]$$
(4)

Where *v* is the Poisson's ratio, *E* is Young's modulus,  $\sigma_x$ ,  $\sigma_y$ ,  $\sigma_z$  are the stresses in x, y, z directions, respectively.

**Figure 2**b shows the stress change of SiTC NPs under particle accumulation. Li source is placed on the outer surface of SiTC NPs, and the particles are lithiated from the outside to the inside. SiTC NPs through point- point contact interaction under the particle accumulation, the tensile stress and reverse stress appear near point-point contact with lithiation process, and the shell of SiTC NPs appear crack at lithiated to 0.74. By analyzing the stress change near the point-point contact (**Figure 2**d), it is found that a large stress gradient change ( $\Delta \sigma$ ) will occur near the point-point contact, which causes the shell to crack. In contrast, the carbon filler increases the contact area between the particles in the model of the progressive stress management strategy, and the TiO<sub>2</sub> layer as a stress management interlayer further alleviates the expansion of Si

particles, which ensures the mechanical structure stability of the Si particles during the lithiation. By analyzing the stress changes of SA-SiTC, it is found that  $\Delta \sigma$  change little, indicating that the Si surface is uniformly stressed. Finally, the hoop stress distribution of SiTC NPs and SA-SiTC under complete lithiation state with 3D modeling simulation. To simplify the calculation, the surface of the SA-SiTC particles is uniformly applied with a gradually increasing stress to simulate the interaction under multiple particles. It can be clearly observed that the Si-based particles in the SA-SiTC structure have relatively low hoop stress. Compared with the SiTC NPs structure, the outward tensile stress of SA-SiTC is reduced by 0.53 times. The change of tensile stress ensures the shape mechanical structure stability of SA-SiTC during the lithiation process, which leads to the stability of the cycling. Therefore, our modeling research provides guidance and optimization for the preparing the functional architectures from a mechanically constrained perspective, while other factors have not been clearly understood, such as formation and evolution of SEI film, (de)lithiation rate effect, and generation of different lithium silicon alloys, et al. These need to be more in-depth research in the future.

To evaluate the structural benefits of the model, we design and synthesize self-assembled hierarchical Si@TiO<sub>2</sub>@C (SA-SiTC) through the guidance of simulating stress evolution, and the process mainly adopts a bottom-up water-in-oil (W/O) reverse microemulsion approach. The schematic of the synthetic SA-SiTC

shown in **Figure 3**, the TiO<sub>2</sub> layer is uniformly coated on the surface of the Si NPs by a facile sol-gel strategy. And the surfactant is induced to shrink to form a self-assembled structure by evaporating the polydisperse water droplets in the oil phase. It is worth noting that the  $TiO_2$  layer is super-hydrophilic under the irradiation of ultraviolet light, which ensures that Si@TiO2 NPs are stable in the aqueous phase during self-assembly. As we previously reported, <sup>[23]</sup> the ethanol solution containing citric acid and silicon-based particles undergoes an esterification reaction during vacuum drying. As shown in Figure S3, the carboxyl group of citric acid and the hydroxyl group of ethanol generate a highly viscous gel by catalysis of silicon-based particles (Figure S4b). The formed highly viscous gel is the triethyl citrate (Figure S2), and the carbon coating prepared by carbonizing a highly viscous gel. As shown in Figure S6a, the primary Si NPs have an average diameter of ~ 70 nm, which facilitates the transport of lithium ions and improves the cycling stability during the (de)lithiation process.<sup>[24]</sup> The obtained Si@TiO<sub>2</sub> NPs are coated by the TiO<sub>2</sub> layer with a thickness of ~3.2 nm. As shown in Figure 4a-c and Figure S7, the obtained SA-SiT has a diameter ranging from 0.5 to 10 µm, and most of the SA-SiT have a completely spherical shape. Figure 4a shows the perfect spherical structure of the SA-SiT, and the surface of the SA-SiT has different sized pores (Figure S7d). These pores can allow for introducing the carbon into the interior of the microsphere and provide adequate space to accommodate the volume expansion of Si during (de)lithiation. Figure 4d-f exhibits the structure of the microspheres is more compact after carbon-coated, the

carbon enters the SA-SiT to fill the pores, the thickness of the carbon layer on the surface of the Si@TiO<sub>2</sub> is about 6 nm (the inset in Figure 4e). And the SA-SiTC shows the complete spherical structure after 10 min intense sonication in cyclohexane (Figure S9). Different from traditional core-shell carbon-coated silicon-based anodes, the carbon in the SA-SiTC is not only coated on the Si particles surface but also filled the pores in the self-assembled structure, building a complete carbon skeleton, improving the conductivity of the electrode material and ensuring structural integrity. As shown in **Figure 5**a, the tap density of SA-SiT is  $0.63 \text{ g cm}^{-3}$  due to the tight self-assembly structure, which is 4.5 times that of Si NPs ( $0.14 \text{ g cm}^{-3}$ ). And the carbon effectively fills the pores of the SA-SiT during the carbon coating process, the obtained SA-SiTC exhibits a high tap density of 0.68 g cm<sup>-3</sup>, which facilitates the high volumetric capacity of the electrode and prepares compacted anode. And SA-SiT can obtain the highest density of  $0.7 \text{ g cm}^{-3}$  (Figure S10) through different centrifugal speeds. The Raman spectrum (Figure 5b) displays the three peaks of 505, 1360 and 1600 cm<sup>-1</sup> correspond to Si-band, carbon D-band and G-band, respectively. The integral area ratio of the D-band to the G-band is 1.3, which indicates SA-SiTC has excellent conductivity.<sup>[25]</sup> XRD (Figure 5c) indicates SA-SiTC consists of Si, anatase and amorphous carbon. X-ray photoelectron spectroscopy (XPS, Figure 5d and Figure S14) also illustrates the coexistence of TiO<sub>2</sub>, Si and C. The Brunauer-Emmett-Teller (BET) of SA-SiT exhibit typical IV curves with H4

hysteresis loops, it is indicated that SA-SiT has a typical slit pore structure. The pore size distribution based on the Barrett-Joyner-Halenda (BJH) method shows that most of the pore size of SA-SiT ranges from 25 to 65 nm (Figure S12), which is consistent with the above SEM results. And the BET analysis (Table S2) of SA-SiTC shows that SA-SiTC has a higher specific surface area than that of SA-SiT, which due to the amorphous carbon deposits in the slit pores and covers the surface of the microspheres. The amorphous carbon has many micropores leading to an increase in specific surface area, which facilitates faster electron diffusion in batteries. Figure 5f reveals the thermogravimetric (TG) curve of the sample under the air atmosphere, SA-SiT is oxidatively stable at < 700 °C due to the action of the TiO<sub>2</sub> protective layer. The continuous weight loss of the SA-SiTC in the range of 450-600 °C, corresponding to the carbon combustion in the SA-SiTC, and the carbon content of the SA-SiTC is about 24 %, which based on the weight change of SA-SiT and the SA-SiTC. Also, the mass content of TiO<sub>2</sub> of SA-SiTC is about 4.5 % according to the calculation result of ICP, and the mass content of Si is about 71.5 %.

The (de)lithiation reactions of the electrode are evaluated by cyclic voltammetry (CV) on a half-cell at a scan rate of  $0.1 \text{ mV s}^{-1}$ , as shown in **Figure 6**a. The CV curves of SA-SiTC show a broad peak at 1.2-0.5 V during the first negative scan, which corresponds to the SEI film formation and the irreversible loss of the electrolyte, this phenomenon disappears in subsequent cycles. <sup>[26]</sup> At the same time, the peak is

gradually increased at < 0.185 V, which is attributed to the alloying reaction of Li<sup>+</sup> with Si. Two different anodic peaks appear at 0.3 V and 0.5 V during the reversed scan, which corresponds to the delithiation process of Li<sup>+</sup> from Li-Si alloy. The anodic peaks gradually increase during the subsequent and become stable in the fifth cycle, which indicates the improved delithiation kinetics. The anodic peak near 1.7 V during the initial discharge scan can be attributed to the redox reaction of anatase TiO<sub>2</sub>, and disappears in the rest cycles because of the large irreversible capacity loss of TiO<sub>2</sub> in the first cycle. <sup>[33]</sup> In addition, an additional cathode peak in the subsequent cycles, which is related to the two-stage Li alloying in the range of 0.30-0.70 V to form two different lithiated states. As shown in Figure S16, the SA-SiTC electrode has an initial reversible specific capacity of ~ 1726.5 mAh  $g^{-1}$  at 0.1 A  $g^{-1}$  (specific capacity with respect to Si is ~ 2397.2 mAh  $g^{-1}$ ), and all specific capacities in this report are based on the total mass of Si, TiO<sub>2</sub>, C in the SA-SiTC. The initial volumetric capacity of the SA-SiTC electrode is maintained at ~ 1174 mAh cm<sup>-3</sup> at 0.1 A g<sup>-1</sup> due to the high tap density, which is 2.1 and 3.4 times that of SiTC NPs and Si NPs, respectively (Figure S15). Si NPs has a large void volume among the Si anodes, resulting in a small tap density and low volumetric capacity. However, due to the space-efficient packing of SA-SiTC, its tap density (0.68 g cm<sup>-3</sup>) is significantly higher than that of primary nanosized particles packed randomly (0.14 g cm<sup>-3</sup>). Therefore, SA-SiTC has a high-volume capacity. And the SA-SiTC shows the reversible capacity of 1122 mAh g<sup>-1</sup> (763 mAh cm<sup>-3</sup>) after 500 cycles at 0.7 A g<sup>-1</sup>, which has 71.3 % capacity retention

from the 3<sup>rd</sup> to 500<sup>th</sup>. In contrast, the capacity retention of SiTC NPs is 26.3% from the 3<sup>rd</sup> to 500<sup>th</sup> at 0.7 A g<sup>-1</sup>. Besides, the SA-SiTC electrode shows a large reversible capacity of ~ 842.6 mAh g<sup>-1</sup> after 1,000 cycles at 2 A g<sup>-1</sup> with 83.7 % capacity retention (as compared to the capacity of the 500<sup>th</sup> cycle). The voltage profiles of SA-SiTC for different cycles are illustrated in Figure 6c. The profile does not change much from the 200<sup>th</sup> to the 500<sup>th</sup> cycle, which indicates the stable electrochemical behavior of SA-SiTC electrode. In addition, the electrode slurry is prepared by PVDF as a binder, and the binder is considered a poor binder of the silicon anode. <sup>[27]</sup> As shown in Figure S18, the self-assembled hierarchical Si@C (SA-SiC) also renders a high initial specific capacity similar to that of SA-SiTC, but the specific capacity gradually decreases in subsequent cycles. The reversible specific capacity of SA-SiC electrode is ~ 610.5 mAh  $g^{-1}$  after 500 cycles at 0.7 A  $g^{-1}$  with a capacity retention of 38.3 %. This difference is due to the  $TiO_2$  shell in SA-SiTC that can be used as a strong fence to provide a stable structural framework, which reduces the risk of Si fracture during (de)lithiation. Figure S19 shows the effect of different carbon contents on the cycle performance in the SA-SiTC electrode, as the carbon content increases, the stability of the electrode is improved, and the optimum carbon content in SA-SiTC is ~ 24%. Among them, self-assembled particles without carbon-filled (SA-SiT) and self-assembled particles with small carbon-filled (SA-SiTC-2) exhibit similar cycling performance, this is due to the lack of sufficient carbon-filled to provide progressive

stress-buffering, and a large stress gradient change between the particles causes the particles to crack, resulting in a decrease in cycle performance.

Excellent CE indicates that Li<sup>+</sup> has excellently reversible during (de)lithiation, and the irreversible capacity loss can be attributed to the decomposition of the electrolyte to form the SEI on the electrode surface, and irreversibly consumes Li<sup>+</sup> in the defects of silicon-based composites. <sup>[28]</sup> As shown in **Figure S17**, the SA-SiTC electrode has a high initial CE (80.9 %) at 0.1 A g<sup>-1</sup>, which is superior to Si NPs (67.8 %) and SiTC NPs (72.3 %), respectively. And the SA-SiTC electrode has higher CE than SiTC NPs in subsequent cycles, SA-SiTC (98.6 %) has a higher average CE than SiTC NPs (98.0 %) during the first 100 cycles. And the average CE of the SA-SiTC electrode is as high as 99.8% from the 200<sup>th</sup> to 500<sup>th</sup> cycle, which is superior to most previously reported (**Table S4**).

**Figure 6**f illustrates the rate performance of the SA-SiTC and SiTC NPs electrodes, both electrodes show similar specific capacity at 0.1 A  $g^{-1}$  and 0.5 A  $g^{-1}$ , but SA-SiTC has excellent rate performance at higher rates (~ 823 mAh  $g^{-1}$  at 6 A  $g^{-1}$ ), while the SiTC NPs has a low specific capacity of ~ 471 mAh  $g^{-1}$  at 6 A  $g^{-1}$ . And when the scan rate is reverted to 0.5 A  $g^{-1}$ , the specific capacity of SA-SiTC can still recover to 1332 mAh  $g^{-1}$ . This is because at the high scan rate (with high current density), the Si NPs will expand faster, and the stress in SA-SiTC will be released in time without causing excessive local stress and cracks. To further clarify the advantages of self-assembled structure in the electrochemical process,

electrochemical impedance spectroscopy (EIS) is performed. The Nyquist plots of SA-SiTC and Si NPs are exhibited in **Figure 6**g and **Figure S22** (fitted by the equivalent circuit as shown in **Figure S23**b), and the semicircle represents the charge transfer resistance R<sub>ct</sub>. The R<sub>ct</sub> of SA-SiTC is significantly smaller than that of Si NPs (**Figure S23**a), which indicates that the surface kinetics of the SA-SiTC is much faster than that of Si NPs. In addition, there is no significant impedance increase, which shows SEI film on the surface of the SA-SiTC has no obvious growth, the excellent stability of the structure is further confirmed during cycling.

The full cells are prepared by using the commercial LiCoO<sub>2</sub> (LCO) and LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) as a cathode to evaluate the practicality of SA-SiTC. To compensate for the first irreversible capacity loss of the Si-based material, the pre-lithiation procedure of the working electrode (SA-SiTC) is conducted in a half-cell, which is lithiated to 0.01 V at 0.2 A g<sup>-1</sup> by constant current (dis)charge (see detail in Methods). The capacity ratio of the anode to cathode the full-cell test is 1.2:1. As shown in **Figure 7**, the SA-SiTC full-cell exhibits a high cycling stability, which displays voltage windows of 2.5 V - 4.4 V and provides a high reversible capacity of ~ 136 mAh g<sup>-1</sup> and 126.2 mAh g<sup>-1</sup> based on LCO // SA-SiTC and NCA // SA-SiTC at 0.5 C (1 C = 0.28 A g<sup>-1</sup>, based on the cathode active material) and a high reversible capacity of 121 mAh g<sup>-1</sup> and 120.4 mAh g<sup>-1</sup> at 1 C. The energy density of the full cell is calculated by the following equation:

$$E = \frac{C_c \times m_c}{m_c + m_a} V_n \tag{5}$$

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Where *E* is the energy density,  $C_c$  is specific discharge capacity of the cathode,  $m_c$  and  $m_a$  are the mass loading of cathode and anode respectively, and  $V_n$  is the average discharge voltage of the full cell.

The full cell can provide high gravimetric energy densities of ~ 394.8 Wh kg<sup>-1</sup> and ~ 362.6 Wh kg<sup>-1</sup> based on LCO // SA-SiTC and NCA // SA-SiTC electrodes in 6<sup>th</sup> cycle, and ~339.9 Wh kg<sup>-1</sup>, 281 Wh kg<sup>-1</sup> in the 100<sup>th</sup> cycle. The full cells of the energy densities are higher than the commercial LIBs (~230Wh kg<sup>-1</sup>). <sup>[29]</sup>

**Figure 8**a and b show schematic illustration of final architecture state SA-SiTC and SiTC NPs after the (de)lithiation. For SiTC NPs structure, the SEI film is formed on the surface of a single nanoparticle. Different from silicon-based particles with an open inner surface, the carbon layer on the outer surface of SA-SiTC acts as an electrolyte-blocking layer that limits most of the SEI formation to the surface of micron-sized particles. This mechanism decreases the quantity of SEI. The SEM image (**Figure S24**a) displays the repeated growth of SEI films can be clearly observed on the Si NPs electrode after 150 cycles. And SEM image (**Figure 8**d) exhibits almost perfect spherical micron-sized particles and uniform SEI film on the surface. The thickness of SA-SiTC electrode is 18.4 μm after 150 cycles, which is only increased by 15% compared to the initial electrode, further demonstrating the structure has higher mechanical stability.

The excellent electrochemical performance of SA-SiTC could be ascribed to the following: (i) primary particles use ~70 nm silicon to prevent the crack; <sup>[24]</sup> (ii) the TiO<sub>2</sub> layer and carbon provide a buffering effect, and the surface tensile stress of the Si is effectively reduced by the interaction between the particles in the unique self-assembled structure, which ensures the mechanical structure stability; (iii) the filled carbon skeleton and the surface-coated carbon layer not only provide fast diffusion path of electron , but also effectively limits overgrowth of SEI film on the surface of the SA-SiTC microspheres, which increases CE and improves cycle stability; (iv) the prepared self-assembled structure with high tap density significantly increases the volumetric capacity of the electrode.

### 3. Conclusions

In summary, we reported a novel strategy that used cross-scale simulation as a stress-management tool coupled with the synthesis of self-assembled hierarchical architecture (SA-SiTC) as anodes for development of high-performance LIBs. Cross-scale simulation allows us to deeper understand the stress evolution of particle interactions during lithiation, and has the possibility to adjust the Si-based building blocks flexibly. Simulation result shows that carbon filler can change the contact mode of Si-based building blocks to limit the stress concentration between particles, and the

surface stress of the Si-based building block can be effectively reduced through the interaction between the particles to achieve the integrity of the particles during (de) lithiation. The unique self-assembled hierarchical architecture based on Si@TiO<sub>2</sub> building blocks prepared by effective stress-management simulation guidance can achieve high performance, including ultrastable cycling stability (842.6 mAh g<sup>-1</sup> after 1000 cycles at 2 A g<sup>-1</sup>), high volumetric capacity (1174 mAh cm<sup>-3</sup>), high initial Coulombic efficiency (80.9 %), which is superior to most previously reported. This work provides insight for the preparation of functional architectures with high volumetric energy density and long cyclic structure stability via effective stress-management. And this strategy has great potential for the development of other high-performance materials for rechargeable batteries.

# 4. Experimental

## 4.1 Synthesis of Core-Shell Si@TiO2 Nanoparticles (SiT NPs)

The core-shell Si@TiO<sub>2</sub> composite was synthesized by a sol-gel coating approach. First, 0.4 g Si NPs (~70 nm, HAOXI Research Nano CO., Ltd.) was homogeneously dispersed by ultrasonication in a mixed solution containing 300 ml absolute ethanol and 1.5 ml 28 % aqueous ammonia. Then, 250 mg titanium isopropylate was added dropwise and aged for 24 h at 40 °C under gentle stirring (200 rpm). After aging, the obtained solution was conducted on 3 rounds of centrifugation/ethanol washing/sonication and dried in a vacuum oven at 100 °C for 10 h, and the obtained

powder was calcined under the Ar atmosphere at 600  $^{\circ}$ C for 2 h with a heating rate of 10  $^{\circ}$ C min<sup>-1</sup>. The final core-shell Si@TiO<sub>2</sub> powder was obtained.

### 4.2 Preparation of Self-assembled Si@TiO<sub>2</sub> (SA-SiT)

The 0.4 g Si@TiO<sub>2</sub> NPs were ultrasonically dispersed in 20 ml distilled water, and the obtained 8 ml water dispersion was mixed to the 32 ml 1-octadecene solution containing 0.5 wt% emulsion stabilizer (hypermer 2296, Croda USA) and mixed at 8000 rpm for 2 min. The mixture was heated in an oil bath at 105 °C for 3 h, and during the oil bath heating process, the solution was irradiated with an ultraviolet light (365 nm) to ensure the superhydrophilicity of TiO<sub>2</sub>. The resulting solution was subjected to 2 rounds of centrifugation / petroleum ether washing and dried in a vacuum oven at 80 °C for 5 h. The obtained powder was calcined at 600 °C for 1 h with a heating rate of 10 °C min<sup>-1</sup> under Ar atmosphere.

# 4.3 Synthesis of carbon coating

4 g citric acid was dissolved in 50 ml absolute ethanol solution to prepare a polymer precursor solution, then 0.4 g the SA-SiT was added in the polymer precursor solution under vigorous stirring for 1 h. The mixture was dried in a vacuum oven at 80 °C for 20 h. After that, the obtained highly viscous gel was carbonized at 600 °C for 2 h under Ar with a heating rate of 10 °C min<sup>-1</sup>. To investigate the effect of different carbon contents, citric acid ranging from 2 to 8 g was added. According to the different amounts of citric acid added, the samples were labeled as SA-SiTC-2, SA-SiTC-4, SA-SiTC-8, respectively.

### 4.4 Character

The structural characteristics of the samples were characterized by transmission electron microscopy (TEM, JEOL JEM-2010-FEF) and scanning-electron microscope (SEM, Sirion 200). The surface chemistry of SA-SiTC was measured by X-ray photoelectron spectroscopy (XPS, AXIS UltraDLD), All peaks were calibrated using reference carbon (C 1s = 284.6 eV). The weight percentage of carbon in the sample was determined by hermogravimetric analysis (Simultaneous DSC-TGA) under air atmosphere with a heating rate of 10 °C min<sup>-1</sup>. The phase compositions are measured by X-ray diffraction (XRD, D8 Advance, Bruker). Raman spectra were obtained using BRUKER/SENTERRA (R-200L) with an excitation at l=633 nm. The highly viscous gel was detected by Gas Chromatography-Mass Spectrometer (GC-MS). Particle size was determined by nanoparticle size analyzer (Zetasizer Nano S). The specific surface area and pore size distribution were determined from the results of the N<sub>2</sub> adsorption/desorption measurement by ASAP 2020 Accelerated Surface Area and Porosimetry (Micromeritics Inc., USA). Inductively coupled plasma atomic emission (ICP, Shimadzu) analyzed of the mass content of Si and  $TiO_2$  in SA-SiT.

4.5 Electrochemical characterization

Electrochemical investigations were carried out using coin-type cells (CR2032). The working electrodes were mixed with 70 wt% active material, 15 wt% Super P (TIMAL, Switzerland) and 15 wt% polyvinylidene difluorides (PVDF, Kynar HSV) 900). Among them, the half-cell anode was coated on a copper foil with a 100 µm spatula and the full-cell anode was coated with a 50 µm spatula. The mass loading of the half-cell anode was  $\sim 1.7$  mg cm<sup>-2</sup> and the mass loading of the full-cell anode was  $\sim 0.8$  mg cm<sup>-2</sup>. The half-cell uses lithium foil as a counter electrode, and the full-cell uses lithium cobalt oxide (LCO) and LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) as the cathode (coated with 80 wt% cathode, 10 wt% Super P and 10 wt% PVDF on the aluminum foil, the mass loading of the cathode was  $\sim 4 \text{ mg cm}^{-2}$ ). All cells were fabricated inside an Ar-filled glove box with Celgrad 2400 as a separator. The electrolyte of the half-cell was LX-025 electrolyte (Suzhou Ganmin Chemical Reagent Co., Ltd.), and the electrolyte of the full-cell was 1.0 M LiPF<sub>6</sub> in 1:1 vol/vol ethylene carbonate/dimethyl carbonate. The anode capacity was 120 % of the cathode capacity in the full cell, and the specific capacity of the full cell was based on the cathode capacity. To compensate for the first irreversible lithium loss, the SA-SiTC anode material was conducted by the prelithiation process. Electrochemical prelithiation was conducted with a pure lithium foil as a counter electrode in the half-cell, which was cycled for 8 cycles at 0.2 A g<sup>-1</sup>. Then the SA-SiTC half-cell was disassembled in a glove box, the pre-lithiated SA-SiTC electrical, and the cathode electrode form a full cell. The cyclic voltammogram (CV) and electrochemical impedance spectrum (EIS)

were conducted on a CHI 660D (Shanghai CH Instrument Co., Ltd.). The electrochemical performance was tested on a Land CT2001A (Wuhan LAND Electronics Co., Ltd.) with a cut-off voltage of 0.01 V - 1.6 V for the half-cell and a cut-off voltage of 2.5 V - 4.4 V for the full-cell. To observe the change of the electrodes, the half-cells were disassembled in a glove box, and the electrodes washed several times with dimethyl carbonate (DMC) to remove residual electrolyte.

### 4.6 Chemomechanical Model

The elastic-perfectly plastic model is used to describe the deformation caused by lithiation, and a nonlinear diffusion model simulats the Li<sup>+</sup> diffusivity of Si particles. The simulation process is performed in Abaques 6.14 / Standard, and model results for 3D structures are post-processed using the software HyperView 14.0. Because the governing equations of thermal and mass diffusion are identical, the coupled temperature-displacement procedure replaces the Li<sup>+</sup> diffusion and stress-strain fileds fields in Abaques 6.14/Standard, that is, the thermal expansion coefficient is used instead of the lithiation expansion coefficient  $\beta_{ij}$ , and the temperature field is substituted for the normalized Li<sup>+</sup> concentration *c*. The NLGEOM option is used to indicate large geometric changes. Meanwhile, the user material subroutine for heat transfer (UMATHT) is used to design the Li<sup>+</sup> diffusivity of Si particles. In the model, it is assumed that the volume of Si after complete lithiation is increased by 280%, the volume expansion coefficient of Si as follows:  $\beta_{ij}$ =0.0038, and the volume of the carbon and TiO<sub>2</sub> is unchanged, the setting value of the material is shown as table S1. The model is the lithiation

process under ideal conditions, the TiO<sub>2</sub> layer and carbon act as a stress management interlayer, which has a uniform Li<sup>+</sup> and a constant modulus, it can provide enough support for the mechanical constraint on the lithiated Si. Generally, the Li<sup>+</sup> diffusion rate is  $10^{-11}$  to  $10^{-6}$ cm<sup>2</sup> s<sup>-1</sup> in carbon-based materials, <sup>[30]</sup> the Li<sup>+</sup> diffusion rate of anatase TiO<sub>2</sub> is  $4.7 \times 10^{-12}$  cm<sup>2</sup> s<sup>-1</sup>, <sup>[31]</sup> and the silicon renders rather low lithium diffusion with the diffusion coefficient between  $10^{-14}$  to  $10^{-13}$  cm<sup>2</sup> s<sup>-1</sup>. <sup>[32]</sup> In the SA-SiTC structure, Li<sup>+</sup> is uniformly transmitted from the carbon surface to the inside, and the transport speed of Li<sup>+</sup> in the carbon and TiO<sub>2</sub> is larger than the lithiation speed of Si particles. In order to ensure that sufficient Li<sup>+</sup> react with Si in the simulation and simple calculation, the diffusion coefficients of the carbon and TiO<sub>2</sub> layers are set to be constant. It is worth noting that our diffusion simulation is mainly used for stress analysis of silicon-based materials, rather than providing an accurate description of the dynamic lithiation process.

### Acknowledgments

We gratefully acknowledge the financial support from National Science Foundation of China (51876052, 51976118) and the Fundamental Research Funds for the Provincial Universities of Zhejiang (GK199900299012-021). We also thank the Instrumental Analysis Center of Shanghai Jiao Tong University for material characterization.

### **Conflicts of interest**

There are no conflicts of interest to declare.

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Figure 1. Mechanism of particle interaction during the lithiation process. (a) Particle

accumulation; (b) Progressive stress management strategy



**Figure 2.** Chemomechanical modeling of stress distribution during lithiation. (a) SiTC NPs, i at lithiation states of 100%; (b) SiTC NPs under particle accumulation, ii and iii

states of 30 % and 100 %; (d) Stress changes near the cracked surface of SiTC NPs during lithiation; (e) Stress change of TiO<sub>2</sub> layer in SA-SiTC during lithiation; (f) Tensile stress change of Si surface during lithiation ~70 nm Ultraviolet light ~0.5-10 um Oil phase Nano-Si Self-Assembly Si@TiO<sub>2</sub> SA-SiT Water phase Carbon coating Microemulsion droplet 0= n Poly(isobutylene) succinic anhydride (Hypermer 2296) Polar hydrophilic Non-polar hydrophilic (water-loving) head (water-hating) head SA-SiTC

Figure 3. Schematic showing the preparation of SA-SiTC

# Author Manuscrip



Figure 4. Morphological and structural characterization. (a-c) SEM and TEM images of SA-SiT. The inset is the HR-TEM image showing that the  $\sim$ 3.2 nm thickness TiO<sub>2</sub> layer; (d-f) SEM and TEM images of SA-SiTC. The inset is the HR-TEM image showing that the  $\sim$  6 nm thickness amorphous carbon layer is coated on the Si@TiO<sub>2</sub> and the slot hole filled with the amorphous carbon



Figure 5. Characterization of SA-SiTC. (a) Tap density; (b) Raman scattering spectra;(c) XRD patterns; (d) XPS survey spectra; (e) Nitrogen sorption isotherms; (f) TGA curves under air atmosphere



**Figure 6.** Electrochemical performance. (a) CV curves of SA-SiTC; (b) Reversible delithiation capacity for the 500 cycles (0.1 A g<sup>-1</sup> for the first two cycles, and 0.7 A g<sup>-1</sup> for the subsequent cycles); (c) Voltage profiles of SA-SiTC at 0.7 A g<sup>-1</sup>; (d) Reversible delithiation capacity of SA-SiTC for the 1000 cycles (0.1 A g<sup>-1</sup> for the first two cycles, and 2 A g<sup>-1</sup> for the subsequent cycles); (e) Voltage profiles of the SA-SiTC at different scan rate; (f) Rate capabilities of SA-SiTC at different rates from 0.1 A g<sup>-1</sup> to 6 A g<sup>-1</sup>;

(g) Nyquist plots of SA-SiTC at different stages of cycling



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Full cell SA-SiTC//LCO

3rd

6<sup>th</sup>

50<sup>th</sup>

20

100<sup>th</sup>

40

60 Specific capacity (mAh g<sup>-1</sup>)

80

Full cell SA-SiTC//LCO

Full cell SA-SiTC//NCA

80

90

100

100

120

140

Voltage (V vs Li/Li<sup>+</sup>)

4.0

3.5

3.0

2.5

2.0

0

60

70



Figure 8. Schematic illustration of the final architecture state upon (de)lithiation. (a) SiTC

NPs; (b) SA-SiTC. Cross-sectional SEM images of SA-SiTC electrode (c) before cycling; (d)

after 150 cycles at 2 A  $g^{-1}$ 

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# Title:

Silicon-Based Self-Assemblies for High Volumetric Capacity Li-Ion Batteries via Effective Stress Management

Date: 2020-08-26

# Citation:

Shi, J., Zu, L., Gao, H., Hu, G. & Zhang, Q. (2020). Silicon-Based Self-Assemblies for High Volumetric Capacity Li-Ion Batteries via Effective Stress Management. ADVANCED FUNCTIONAL MATERIALS, 30 (35), https://doi.org/10.1002/adfm.202002980.

Persistent Link: http://hdl.handle.net/11343/298005