



## Low-cost open-space scaffold structure for high-capacity silicon anode

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### A B S T R A C T

One of the causes of capacity fading in cells containing silicon anodes is the growth of a secondary SEI. A possible way of solving this problem is to create an anode with a highly porous three-dimensional structure, in which the growing SEI could be accommodated without blocking conduction pathways inside the anode. We evaluated this approach by building a 3D carbon-fiber (CF) scaffold matrix made by the pyrolysis of cotton wool. Anodes fabricated from bare and carbon-coated silicon nanoparticles, were studied from the viewpoint of the influence of anode structure and  $\text{Li}_x\text{Si}$  phase transformations on prolonged cycling of Li/Si cells. Analysis of the mechanisms of degradation of silicon anodes in lithium-ion batteries provides possible ways of elimination of the negative effect of the growth of the SEI on capacity fading. It will be noted that all the anodes containing cotton-carbon fiber matrix exhibit much more stable cycle life than do CF-free anodes. The synthesis of the carbon-fiber (CF) scaffold matrix is simple and easy to scale up to industrial production.

### 1. Introduction

In order to increase the energy density of the lithium battery, better anodes and cathodes are required. Silicon has attracted much attention because its theoretical capacity is 4200 mAh/g [1], an order of magnitude greater than that of graphite. The lithium-rich silicon compounds have high melting points and their higher working potentials (vs. Li), than those of graphite, avoid the possibility of metallic-lithium deposition caused by overcharge. Silicon is the second-most abundant element in the earth's crust, and it is environmentally benign. Yet, the main disadvantage of this high-capacity anode material is poor capacity retention of the cell, which is caused by very large volume expansion and contraction (~280%) during lithium insertion/de-insertion. Cracking and pulverization of active anode material and conductive matrix and their separation from the current collector could follow the volumetric changes [2]. In [3] it was found that the SEI composition and thickness in lithiated and delithiated state of the graphite anode differ after 3 cycles, and that the thickness of the SEI increases up to 50 cycles. Since the steady state is reached after 50 cycles, the authors assert that the SEI on graphite is dynamic. The changes occurring on silicon anode surface are much stronger. Because of the extreme volume change of the silicon alloy anode on cycling, the SEI film tends to break frequently, thus exposing the free surface of the anode to further reduction of the electrolyte. This is followed by the formation of a fresh, compact and secondary porous SEI [4]. High irreversible capacity and poor faradaic efficiency (FE) arise from these phenomena [5]. Huang

et al. showed that there is a critical particle diameter of ~150 nm below which cracking did not occur at the lithiation stage, and above which surface cracking and particle fracture took place [6,7]. Synthesized silicon nanostructures, including nanowires [8], nanocrystals [9], core-shell nanofibers [10] and silicon/carbon nanocomposites [11] have demonstrated superior performance as compared to bulk silicon. However, the synthesis of nanomaterials, and nanowires in particular, typically requires complex methods and expensive instruments, such as CVD and plasma spray PVD.

In this work, an attempt was made to reduce the degradation of the Si/carbon nanocomposite anode by the preparation of a highly porous three-dimensional carbon-fiber scaffold matrix, in which the SEI growth could occur without blocking conduction pathways inside the anode. The carbon-fibers were produced by the pyrolysis of cotton wool. The cotton wool was chosen by virtue of its curved structure, abundance, low cost and the fact that it does not require prior polymerization, thereby avoiding environmental pollution and additional energy consumption.

A major guideline in our work is that the anode should be low-cost and easy to scale up. Therefore, the developed anode was fabricated by the traditional doctor-blade technique used in the battery industry.

### 2. Experimental

Spherical silicon nanoparticles (SiNPs) with a median diameter,  $D_{50}$ , of 100 nm were purchased from Umicore. SiNPs coated by carbon were

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prepared as follows: 1.1 g of sucrose (22%w/w) and 3.9 g of SiNPs (78% w/w) were dispersed in 75 ml of deionized water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ). The suspension was mixed in a high-power ultrasonic homogenizer for 30 min, 0.4 ml of triton X-100 (TRX) (Sigma) was added, followed by additional mechanical stirring to form a homogeneous suspension. The water was then evaporated at  $80^\circ\text{C}$  in order to obtain a solid blend. The blend was subjected to pyrolysis for an hour under an argon/hydrogen gas mixture (96%/4%) at  $1000^\circ\text{C}$  in a Carbolite TZF 12/65/550 oven. The heating rate was  $5.5^\circ\text{C}/\text{min}$  and the gas flow rate was  $50 \text{ cm}^3/\text{min}$ . The product obtained was ground by mortar and pestle into smaller particles and labeled as SiNPC.

Medical-grade cotton wool (10 g) was pyrolyzed under the same conditions. After a dwell time of 2 h, the carbon was cooled under an argon/hydrogen mix of gases. The product of pyrolysis, in the form of a soft and fluffy black lump, was washed with acetone and ethanol and labeled Carbon Cotton Fiber (CF). The yield of the process was approximately 10%. The BET area of CFs was about  $500 \text{ m}^2/\text{g}$  with the average pore size of  $40 \text{ \AA}$ . Then, 830 mg of CF was functionalized in a mixture of concentrated nitric and sulfuric acids. 50 ml of  $\text{HNO}_3$  (70%(w/w)) and 150 ml of  $\text{H}_2\text{SO}_4$  (98%(w/w)) were mixed in an Erlenmeyer flask that was then heated on a hot plate to a temperature of  $60^\circ\text{C}$ . CF was softly ground to a powder by mortar and pestle, added to the flask, and stirred for 2 h. The powder was then washed with deionized water, and filtered until the washed water reached the pH 5.5.

For the electrochemical tests, the electrodes were prepared as follows. Lithium polyacrylate (LiPAA) was prepared from poly(acrylic acid) MW = 1,250,000 g/mol (Scientific Polymer Products, USA) with a stoichiometric amount of  $\text{Li}_2\text{O}$  or LiOH for full neutralization. A binder, (sodium carboxymethyl cellulose (NaCMC, BDH Laboratory Reagents, England) or a home-made LiPAA- was dissolved in an aqueous solution under stirring. SiNPs or SiNPC were added to the solution containing binder and stirred until a homogeneous slurry was obtained. The carbon additives, CF, KS6, multiwall and single-wall carbon nanotubes (MWCNTs and SWCNTs, SkySpring and OCSiAl) were added to the slurry. The MWCNTs were pre-functionalized by the mixture of acids, as mentioned elsewhere [12]. The slurry was spread on  $20 \mu\text{m}$ -thick copper foil (Schlenk, Germany) by a doctor-blade technique and was dried under vacuum at  $100^\circ\text{C}$  for 2–3 h. The coin-type 2032 cells were assembled in an argon-atmosphere glovebox, with lithium foil (Rockwood Lithium) as the counter electrode, a composite silicon anode and two 2400 separators (Celgard) immersed in 1M LiPF<sub>6</sub> EC:DEC:FEC (1:1:1 v/v) electrolyte. Galvanostatic cycling was performed with a BioLogic VMP3 system, or a Maccor series 2000 battery-test system, or Arbin cycler. Galvanostatic voltage cutoffs were 0.05 and 1 V vs. Li/Li<sup>+</sup> and the typical C rate was c/4 at charging (delithiation) and c/10 at discharging (lithiation). The composition of the tested anodes is presented in Table 1. The specific capacity values are calculated taking into account the total mass of the anode composite, which includes the active material, carbon additives and the binder.

### 3. Results and discussion

SEM images in Fig. 1 show the morphology of cotton fibers that underwent the pyrolysis. The carbon cotton fibers obtained are several micrometers thick and preserve spiral structure. Carbon cotton has a more undulate shape as compared to the straight rigid carbon fibers typically used in industry, such as PAN-precursor carbon fibers.

We tested two types of silicon nanoparticles in the composite silicon-based anodes. In the first one, the silicon nanoparticles were used as purchased. In the second, the silicon was carbon-coated by pyrolysis with sucrose as a precursor, according to the procedure developed in [11]. CF, KS6, MWNTs and/or SWNTs were used as carbon additives.

Mixing carbon cotton with bare SiNPs in aqueous solution is followed by phase separation which is due to the hydrophobic nature of the surface of the fibers. To overcome the phase separation the fibers

**Table 1**  
Composition of the tested anodes.

Lithiation/delithiation current ( $\mu\text{A}$ ) at different cycles	Electrolyte	Mass loading ( $\text{g}/\text{cm}^2$ )	Anode composition (% w/w)	Cell label
1–150 9–230/575	1 M LiPF <sub>6</sub> EC:DEC:FEC (1:1:1)	1.9	55% SiNPs, 35% CF, 10%NaCMC	CC-SiNPs/ Li
1–70/70 6–240/600	"	1.4	55% Si(C), 35% CF, 10%LiPAA	CC-Si(C)/ Li
1–100 9–172/432	"	1.4	55% Si(C), 30% CF, 5% MWNT, 10% LiPAA	CC-Si(C)- MWNT/Li
45	1 M LiPF <sub>6</sub> EC:DEC (1:1)	1.1	43% SiNPs, 40% SB carbon, 10% MWNT 7%NaCMC	MWNT- SiNPs/Li
1–100 6–160/400 172–50	1 M LiPF <sub>6</sub> EC:DEC:FEC (1:1:1)	1.1	55% Si(C), 35% KS6, 10%LiPAA	Si(C)-KS6/ Li
1–60 5–200/500 146–20	"	1.0	50% Si(C), 30% CF, 10% KS6, 7%LiPAA, 3%NaCMC	CC-Si(C)- KS6/Li
Cycle 1–80 Cycle 5–100/ 250 Cycle 329–10	"	1.1	50% Si(C), 30% CF, 10% KS6, 0.25% SWNT, 7%LiPAA, 3%NaCMC	CC-Si(C)- KS6- SWNT/Li

were treated with a mixture of nitric and sulfuric acids. This was done in order to form carboxyl and other oxygen groups on the CF surface, which can interact with  $\text{SiO}_2$  that covers the SiNP. The surface roughness of the fibers treated by acids increases (Fig. 1b). We have found that the attachment of bare SiNPs to the CF surface is poorer when LiPAA, as opposed to NaCMC, is used as the anode binder. It is worth mentioning that carbon-coated silicon nanoparticles (SiNPC) enable mixing with untreated CF to produce a uniform anode, independent of the type of binder.

SEM images of the composite SiNPC-based anode with NaCMC binder reveals very porous structure with fiber length ranging from 50 to  $200 \mu\text{m}$  (Fig. 1c). As seen in Fig. 1d, silicon nanoparticles cover the carbon-cotton fibers uniformly, and exposed neat fiber surface cannot be distinguished. As mentioned above, LiPAA binder provides a good connection of the carbon-coated-silicon nanoparticles to the surface of the CF fibers, which creates a conducting matrix (Fig. 1f and g). This affinity of the particles to the fiber surface makes for a preferred electrode structure with desirable inner open voids as can be seen from the cross-sectional SEM image (Fig. 1e).

We found that adding 5%(w/w) of MWCNTs to the paste markedly reduces the adhesion of SiNPs to the fiber (Fig. 1h), and as a result, particles accumulate at the bottom of the anode, causing a non-homogeneous, low-porous anode structure. We suggest that, as with the SiNi anode [11], the MWNTs wrap the carbon-coated silicon particles, thus preventing close contact between fibers and nanoparticles.

Electrochemical characterization of Li/Si cells was carried out in 1M LiPF<sub>6</sub> EC:DEC:FEC electrolyte. FEC was added since it was found to be the most effective additive for extending the cycle life of Si-anode cells [12]. This is due to the formation of a kinetically stable SEI comprising predominately lithium fluoride and lithium oxide [13].

The anode composed of a mixture of SiNPs and MWCNT, shows very poor electrochemical performance with a dramatic capacity fade over 20 cycles from  $1055 \text{ mAh}/\text{g}_{\text{anode}}$  at the first delithiation to  $100 \text{ mAh}/\text{g}_{\text{anode}}$  at the twentieth (black curve, Fig. 2a). Whereas the high-porosity anode, composed of SiNPs (blue curve) and the low-porosity anode (Fig. 1) composed of SiNPC (green curve), exhibit much lower degradation rates (0.85%/cycle for the first 50 cycles). The reversible capacity of the neat Carbon Cotton –LiPAA anode has high irreversible capacity of  $260 \text{ mAh}/\text{g}$ . The reversible capacity of Li/CF cell varies from 140 to  $125 \text{ mAh}/\text{g}$  at 50 and  $150 \text{ mA}/\text{cm}^2$  charge/discharge current

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