



Three-dimensional architecture of lithium-anodes made from graphite fibers coated with thin-films of silicon oxycarbide: Design, performance and manufacturability



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HIGHLIGHTS

- Thin films of SiCO on graphite fiber-mesh create a ready-to-go anode for lithium ion batteries.
- The composite performs significantly better than predicted by rule-of-mixtures.
- Both electrochemistry and ab-initio calculations suggest a role for the graphite-SiCO interface.
- The one-step manufacturing of the anodes can be cost-effective and conducive to scale-up.
- The gravimetric/volumetric capacities depend on the diameter and the packing of fibers.

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ABSTRACT

Silicon oxycarbide (SiCO) is an amorphous molecular network of Si–C–O tetrahedra anchored to graphene-like carbon. The graphene forms a three dimensional cellular network with a domain size of ~5 nm. Therefore nanometer thick films of SiCO grown on graphite may be expected to have unusual behavior. We grow these films on a bed of commercially available graphite fibers that serve the dual function of a current collector. The electrochemical behavior of the composite is measured as a function of the thickness of the SiCO films. Thick films approach the typical behavior of bulk SiCO (which has three times the capacity of graphite, but suffers from poor first cycle efficiency). However, films, approximately 100 nm thick, show high first cycle efficiency as well as high capacity. The composite performs better than the prediction from the rule-of-mixtures, which further substantiates the unusual behavior of the thin-film architecture. The Raman spectra of these thin films also differ from bulk SiCO. The development of thin graphite fibers, with a high surface to volume ratio that have the same capacity as the current graphite-powder technology, coupled with manufacturing of these thin-films by a liquid-polymer precursor based process, can propel these results toward commercialization.

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1. Introduction

The silicon-oxycarbides (SiCO) are a relatively new anode material for Li-ion batteries. They have the following special attributes,

- (i) Their capacity ranges from 500 to 1000 mAh g⁻¹, which varies with the molar concentrations of the constituents [1], with the highest values being obtained near the middle of the C–Si–O composition triangle – since they are

amorphous and their composition varies, their capacity cannot be prescribed a theoretical value.

- (ii) They have a pseudo-amorphous, molecular network structure constructed from a cellular graphene-like carbon, with a domain size of ~5 nm. Tetrahedral units of silicon, carbon and oxygen are anchored to the graphene [2]. Thus at the molecular level they comprise a combination of silicon, carbon and SiO_x, which, on their own, are candidates for anode materials. An analysis of Li-capacity data spanning a wide range of compositions, coupled with a nanodomain model for the structure of SiCO compounds, has shown that their high capacity arises from the migration of Li to the mixed-bond C–Si–O tetrahedral units [3].

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- (iii) SiCO materials have low density, typically 2 g cm^{-3} , and, therefore, an open molecular network, which enhances the diffusivity of Li within it [4], leading to good performance at high C-rates [5]. The low modulus and low volumetric expansion upon intercalation, which has been measured to be less than 8% (unpublished), endows very good cyclic stability and high resistance to failure. The chemical inertness of SiCO promotes safety.
- (iv) The silicon oxycarbides are made from silicone resins, also known as siloxanes and silsesquioxanes. The silicon-carbon-oxygen chemistry is built into these liquid polymers and can be varied widely [6]. They convert to the inorganic phase when heated to 800–1000 °C. Thus they are potentially low cost, not only as raw materials, but also from the point of view of manufacturability. The liquid polymer route can open the way for fabricating nanocomposites of various kinds – for example by mixing the precursor with particles of silicon – to further improve performance.

Up till now SiCO has been implemented as anodes in powder form. The polymer precursor is cross-linked by heating to ~ 300 °C, milled into powders and then pyrolyzed by heating in an inert atmosphere at ~ 800 °C, which are then processed into anodes in the same way as graphite powders. The SiCO powders show high capacity with three times the capacity of graphite, good C-rate performance, and cyclic endurance, but suffer from low first cycle efficiency (65%–75%), and large hysteresis between charge and discharge cycles (0.75 V–1.25 V) [7]. Since the intrinsic structure of these materials consists of graphene networks on the scale of ~ 5 nm, we wondered if films of them grown on graphite may lead to better properties. (Earlier work on thin films deposited on copper substrates did not show an improvement [8].) At the same time a novel processing approach also presented itself where we were able to deposit thin films of SiCO using a flash-pyrolysis method where a small amount of the liquid precursor was sprayed onto a web of carbon fibers and pyrolyzed in just a few seconds at 800 °C [9]. The nearly perfect wetting of all surfaces of the fibers within the fiber-matt allowed all fibers to be immediately covered with thin films of SiCO. Films of nanometer thicknesses could be made by diluting the polymer precursor in a solvent and reducing the amount of this solution sprayed on to graphite-fiber matt. Successive cycles of deposition, repeated in quick succession, could be used to build up the film thickness to the desired level.

The choice of graphite fibers in these experiments was limited by those available off-the-shelf. These widely available fibers are optimized for making graphite-reinforced-polymer-composites for structural applications; they are far from being optimized for Li sequestration. In the experiments reported below, we have therefore characterized their electrochemical behavior, as a baseline for the evaluating the results after they have been coated with thin films of SiCO. The premise of these experiments was that the nature of the interface between the graphite and the SiCO films grown on it may influence the structure of the films. Thus the synergy between the fibers and the coatings are studied in two ways, (i) first by increasing the thickness of the coating, expecting that whereas thick coatings would tend toward the bulk behavior of SiCO, thin coatings may reflect the nature of the graphite-SiCO interface, and (ii) by adding the Li capacity from the fibers and from the coating using the rule-of-mixtures, to see if the thin-film behavior deviates from it.

2. Preparation of the anodes

The anodes were prepared with Toray TGP-H-030 graphite paper. According to the manufacturer the fiber mesh has only 20% fill

density, with an overall physical density of 0.4 g cm^{-3} . The fibers are impregnated with a polymer resin. The paper is specified to have a flexural strength of 40 MPa, and flexural modulus of 8 GPa. The average fiber diameter was $7 \mu\text{m}$. The polymer residue in these fibers (5% PTFE) was removed by heat-treating at 1000 °C in argon for 1 h. Coupons, 0.5" in diameter, were punched from the fiber-fabric. The fiber mesh was brittle and fragile after this heat treatment procedure. The coupons weighed 6.5–7.0 mg apiece.

The polymer precursor for SiCO, 1,3,5,7-tetramethyl-tetravinylcyclotetrasiloxane (TTCS) was purchased from Gelest, USA. It was mixed with 1 wt% dicumyl peroxide, which served as a catalyst for cross-linking. If needed the precursor was diluted with THF, a common solvent.

The SiCO-GF anodes were prepared in the following way. A drop of the precursor solution was placed on the fiber coupon. It spreads immediately overall surfaces of the fibers in the mesh. It is then cross-linked at ~ 170 °C, and finally pyrolyzed at ~ 800 °C when it converts into the amorphous SiCO ceramic phase. The last step was carried out in two ways, (i) by gradually heating the specimen, at a rate of $10^\circ \text{C min}^{-1}$ to the pyrolysis temperature, and holding for 5 h in argon atmosphere, and (ii) by flash pyrolysis where the specimen was exposed to approximately 800 °C under a radiant furnace for a few seconds. The latter process was conducted within a glove box in an argon atmosphere with oxygen content of less than 1 ppm. Both methods gave identical electrochemical behavior. Before the coating was applied the 0.5" diameter coupons were fragile, but after the coating they were mechanically resilient and could be bent without fracture.

The thickness of the coating could be anticipated by the following analysis. We write the coating thickness as δ , the fiber-diameter as d , and the weight fraction of SiCO as w_S , the density of graphite and SiCO as ρ_G and ρ_S . Consider a single fiber of a unit length; its weight is given by $\pi(d^2/4)\rho_G$. Since $\delta \ll d$, the weight of the coating is given by $\pi d \delta \rho_S$. Therefore,

$$w_S = \frac{\pi d \delta \rho_S}{(\pi d^2/4)\rho_G + \pi d \delta \rho_S} \quad (1)$$

Rearranging Eq. (1) leads to the following result

$$\frac{\delta}{d} = \frac{1}{4} \frac{\rho_G}{\rho_S} \frac{w_S}{1 - w_S} \quad (2)$$

The fiber diameter was approximately $7 \mu\text{m}$. Therefore w_S of 5%, and 10%, translates into $\delta = 100$ nm and 200 nm, setting $(\rho_G/\rho_{\text{SiCO}}) \approx 1$ since both have a density in the 2.0 – 2.3 g cm^{-3} range.

Micrographs of the graphite mesh before and after coating with 11 wt% SiCO, along with their Raman spectra are shown in Fig. 1. The enhanced contrast in Fig. 1(b), relative to bare fibers in 1(a), is most likely induced by the greater electron reflectivity of higher molecular weight SiCO. The Raman spectrum of the coated fibers is remarkably different from that of the bare fibers. The coating shows a sharp G peak, with broad shoulders that reach far, while the fibers show the characteristic D and G peaks of graphite. The Raman spectrum for SiCO [10] is included in 1(c); it is similar to that of the graphite fibers. In summary the dual D and G peaks seen in powder-SiCO, are replaced in the SiCO films by a single G peak with broad reaching shoulders on either side of the peak.

3. Electrochemical testing

The coupons prepared in the way described above are ready for electrochemical testing since the graphite fibers also serve as the current collector; the mesh makes electrical contact with the bottom cap in the CR2032-type coin cell. The liquid electrolyte permeates through the entire thickness of the electrode. Lithium-

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