



A porous silicon–carbon anode with high overall capacity on carbon fiber current collector

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ABSTRACT

A porous silicon–carbon anode on a lightweight carbon fiber current collector is reported here for lithium-ion batteries. This Si–C anode was synthesized through a one-step carbonization of a Si-poly(acrylonitrile-co-methyl acrylate) precursor, which was directly deposited on a carbon fiber mat. The carbon fiber current collector allows higher loading of active materials, resulting in high energy to mass and area ratios. The obtained Si–C electrode demonstrated superior overall capacity, cyclability, and rate capacity.

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1. Introduction

Lithium-ion batteries are arguably the most promising answer to emerging demands for effective energy storage devices. However, current Li-ion batteries require holistic improvement to achieve higher energy and power densities. One of the limiting factors is the low specific capacity of graphite anodes. To achieve high anodic capacity, silicon is an excellent material because of its high theoretical capacity. However, Si-based anodes suffer from poor cyclability due to drastic Si volume changes during Li insertion/extraction, which cause pulverization of the Si particles. Even when pulverization is alleviated by using Si nanoparticles, a tendency toward poor cyclability remains. Researchers eventually realize it is a direct cause of the compromised mechanical integrity of the electrode due to the repeated Si volume change [1].

As a result, substantial efforts have been devoted to developing Si electrodes with improved mechanical properties. Silicon–carbon composite anodes were extensively studied, due to carbon's conductivity and its ability to accommodate Si volume changes [1–14]. However, most current Si–C anodes merely employ carbon as a coating layer on Si particles. Such a carbon layer improves the charge transfer kinetics, but it cannot improve the mechanical stability of the electrode structure.

Recently, it was reported that porous carbon structures can more effectively accommodate the Si volume change than carbon-coated Si anodes [1,11,15]. We have fabricated porous Si–C anodes by spraying PVDF-Si slurry onto a Cu current collector, followed by carbonization

[15]. This Si–C composite could retain 1280 mAh g⁻¹ capacity after 118 full cycles between 0 V and 1.5 V [15]. However, the thickness of the Si–C film (i.e. active material loading) is limited to less than 10 μm, because the thick Si–C film would flake off during carbonization due to the mismatch between the coefficients of thermal expansion (CTE) between active material and Cu. To enhance the energy density of the Si–C anodes, the Cu current collector should be replaced by a lightweight current collector with a CTE similar to that of the active materials. Commercial carbon paper consisting of carbon fibers has been used as a current collector for tin-based intermetallic compound anodes [16,17]. However, the large pore sizes and fiber diameters (10 μm) in the carbon paper limited their cyclability [16,17].

In the present study, a mixture of Si nanoparticles and carbon precursor polymer was incorporated into a carbon nanofiber mat current collector, followed by carbonization, to directly form a porous Si–C electrode. The entire electrode was synthesized using a one-pot carbonization process, thus eliminating polymer binders. The high Si loading enhances both volumetric and gravimetric energy densities of the electrodes. The obtained electrode demonstrated better capacity, cyclability, and rate performance, evidencing improved structural integrity.

2. Experimental methods

Silicon nanoparticles (20 to 30 nm) were purchased from Nanostructured & Amorphous Materials, Inc. Poly(acrylonitrile-co-methyl acrylate) (PAN-co-PMA, acrylonitrile ~94 wt.%) was purchased from Sigma-Aldrich and used as received. The carbon nanofiber mat was donated by eSpin Technologies, Inc. Si nanoparticles and carbon black (CB) was blended into a 3 wt.% solution of PAN-co-PMA (in *n*-methyl-2-

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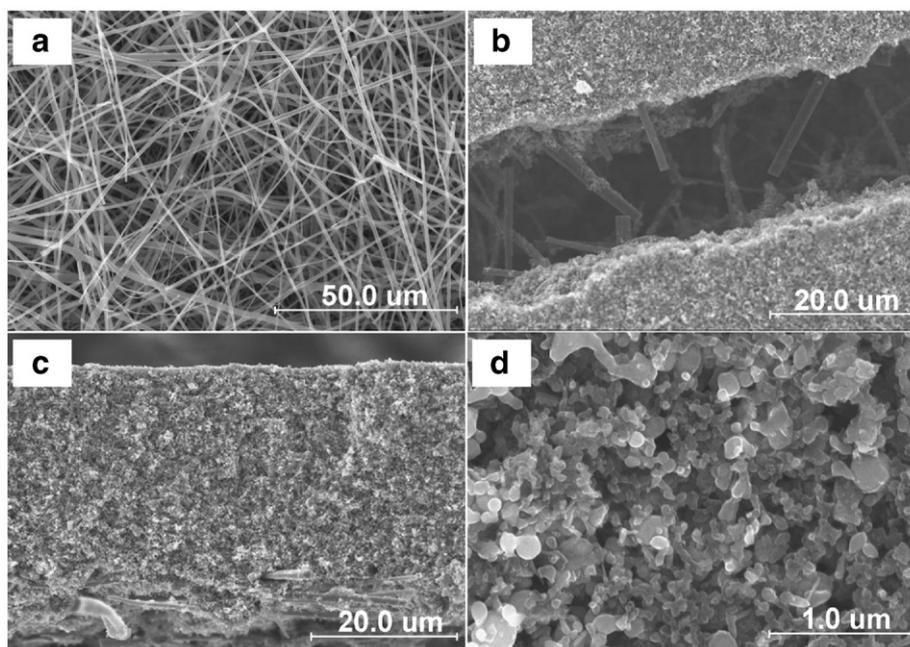


Fig. 1. SEM images of (a) the carbon fiber sheet, (b) the Si-C electrode, intentionally ruptured to show the carbon fiber current collector, (c) the cross-section of the Si-C electrode, and (d) the porous electrode structure at high magnification.

pyrrolidone) to obtain a composition of 50/35/15 ratio of Si/PAN-co-PMA/CB using a mixer (Spex 8000 M) for 1.5 h. The resulting slurry was coated onto and into the carbon fiber mat with a doctor blade. After drying in the fume hood and the vacuum oven for 24 h, the obtained electrode precursor was carbonized at 700 °C for 3 h in a tubular furnace under flowing argon (95% Ar, 5% H₂) to obtain the Si-C electrode on a carbon nanofiber current collector.

For the electrochemical analysis, two-electrode coin cells (2032) with lithium foil as counter electrode were used. Electrolyte consisting of 1 M LiPF₆ in a solution of ethylene carbonate/diethyl carbonate (1:1 by volume) was used with a micro-porous separator (Celgard®3501). The cells were discharged (Li-ion insertion) and charged (Li-ion extraction) at different currents between 0.05 and 1.5 V (vs. Li/Li⁺) using an Arbin battery test station.

Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (Perkin-Elmer) with a heating rate of 5 °C min⁻¹ in air to determine the Si composition in the electrode. The structure and morphology of the electrodes were evaluated using Scanning Electron Microscopy (Hitachi SU-70 SEM).

3. Results and discussion

The electrical conductivity of the carbon nanofiber mat was $1 \times 10^{-3} \text{ S cm}^{-1}$ measured with four-probe method. The average thickness of the carbon nanofiber mat is 150 μm, and it has a uniform density of 2.6 mg cm⁻², which is almost 4 times less than commercial carbon paper (10 mg cm⁻²) [16,17] and 5 times less than an industrial Cu current collector (11.8 mg cm⁻²) provided by Saft America. The SEM image of the carbon nanofiber mat is shown in Fig. 1a. The porous structure of the mat allows high electrode material loading with better electrode-current collector adhesion. It was observed that electrode material thickly coated onto Cu current collectors would flake off after the carbonization process, while electrodes on carbon nanofiber with the same loading ($\sim 2 \text{ mg Si cm}^{-2}$, typical thickness is 40 μm as shown in Fig. 1c) could retain good adhesion after the carbonization. There are two plausible reasons for the better adhesion: the CTE of the carbon nanofiber mat is probably similar to that of the electrode material, as they both contain carbon, and the porous structure of the carbon

nanofiber mat could alleviate some of the strain/stress from the thermal expansion. Fig. 1b shows the surface of the Si-C electrode, which was intentionally broken to show the carbon nanofiber underneath the electrode material. The cross-section shown in Fig. 1c exhibits the

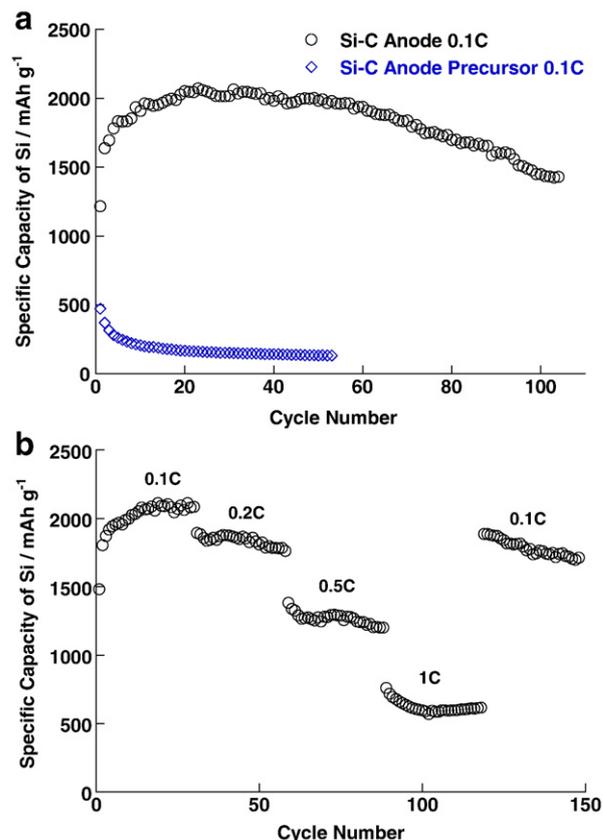


Fig. 2. (a) Electrode capacity per mass of Si cycled at 0.1 C and (b) Si charge rate performance of the Si-C porous electrode.

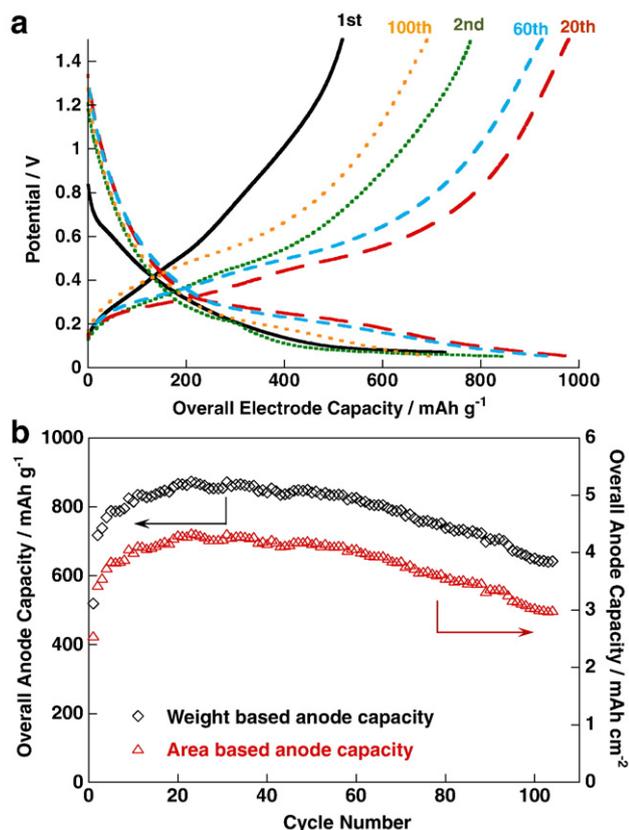


Fig. 3. (a) Galvanostatic charge–discharge curves and (b) overall electrode capacity of the Si–C porous electrode on carbon fiber current collector cycled at 0.1 C.

vertical structure of the Si–C electrode with partial penetration into the carbon nanofiber mat. The deposition of active materials into the carbon nanofiber mat integrates the electrode and the current collector, enhancing the interfacial integrity. The high magnification image in Fig. 1d reveals the porous structure of the Si–C electrode.

The Si composition is 36 wt.% of the total weight of the electrode including current collector, determined by the TGA analysis. Fig. 2a shows the charge (delithiation) capacity retention of the Si particles. The cyclability curve indicates an activation process in the initial cycles. The capacity increased to a maximum at about the 20th cycle. The lower capacity in the first few cycles can be attributed to an initially higher polarization due to the carbon layers on the Si particles surface obtained from the carbonization [10]. After further cycling, the carbon layer became more facile for Li-ion transport, resulting in increased capacity. A capacity of 1400 mAh g⁻¹ was retained after 100 cycles at a 0.1 C charge/discharge rate (200 mA g⁻¹). For comparison, the cyclability of the precursor (prior to carbonization) of the Si–C electrode is also shown in Fig. 2a. It can be seen that the precursor anode shows much lower capacity and worse cycle stability. The porous Si–C electrode also exhibits high rate capacity, as indicated by Fig. 2b. The electrode was cycled consecutively at 0.1 C, 0.2 C, 0.5 C, and 1 C for a total of 150 cycles, and it could retain 600 mAh g⁻¹ capacity at the 1 C rate (2 A g⁻¹). The impressive cyclability and rate capacity of the porous Si–C electrode can be attributed to the carbon matrix obtained from carbonization. The Si–C electrode was synthesized as a whole with better structural integrity. It was able to absorb the Si volume change and retain the stability of the electrode. A similar conclusion was drawn by a previous study [1].

Another advantage of this Si–C electrode is its high overall (including current collector) capacity. Fig. 3a shows the voltage profiles of the 1st, 2nd, 20th, 60th, and 100th cycles. The first overall discharge capacity is 728 mAh g⁻¹, and the first charge capacity is 519 mAh g⁻¹. Therefore, the irreversible capacity of the first cycle is 28.8%. It is notable that the carbon nanofiber mat (30 wt.%) contributes less than 10% of total capacity (carbon nanofiber mat capacity: 228 mAh g⁻¹). The overall discharge and charge capacities in the second cycle are 781 mAh g⁻¹ and 848 mAh g⁻¹. After the second cycle, the coulombic efficiency quickly increases to over 98%. Fig. 3b shows the overall electrode capacity on both a mass basis and an area basis under a 0.1 C rate. After 100 cycles, the Si–C electrode can still retain an overall capacity of 650 mAh g⁻¹ or 3 mAh cm⁻².

To demonstrate the superiority of the Si–C electrode, the electrode was extracted from the coin cell after the cyclability test inside a glove box. The morphology of the surface and cross-section was evaluated

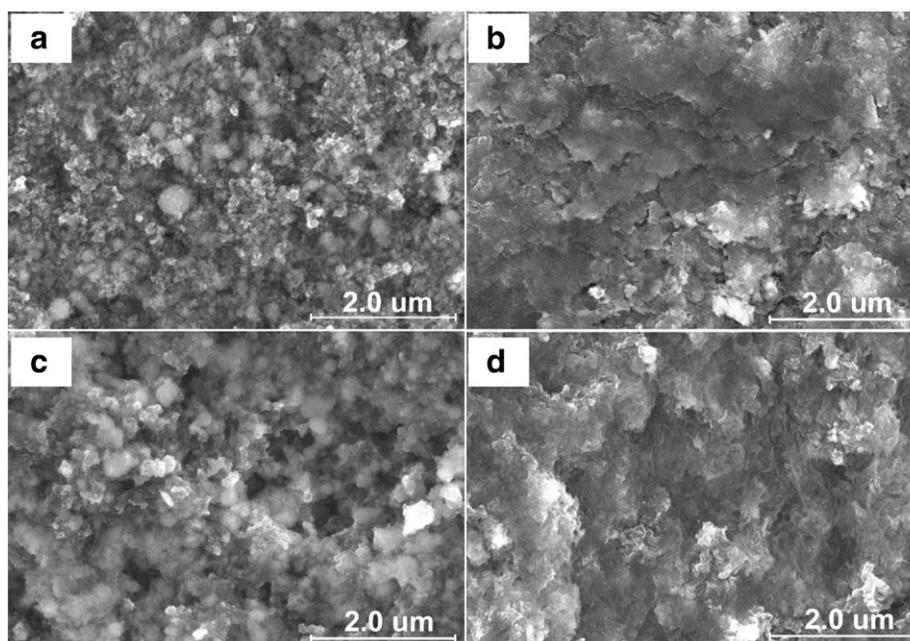


Fig. 4. SEM images of the surface morphologies of (a) the porous Si–C electrode and (b) the precursor electrode and cross-section morphologies of (c) the porous Si–C electrode and (d) precursor electrode.

using SEM and compared to the corresponding areas of the cycled precursor electrode without carbonization. Fig. 4a and b are the surface morphologies of the Si–C electrode and the precursor, respectively, and Fig. 4c and d are the corresponding cross-section morphologies. It is clear that the surface and the entire structure (from the cross-section) of the precursor electrode were covered with SEI film. On the contrary, although the SEI film can also be seen in the Si–C electrode, its original structure can still be distinguished. This observation suggests that the carbon matrix of the Si–C electrode obtained from carbonization is able to facilitate formation of a stable SEI film, thus improving the cyclability.

4. Conclusion

In this study, a porous Si–C anode was synthesized on a lightweight carbon nanofiber current collector. This electrode demonstrated good cyclability, rate capacity, and high overall capacity. Our unique carbonization method synthesized the electrode directly on the current collector. The advantage of this Si–C electrode is its high structural integrity, owing to the one-piece carbon framework for the entire electrode. The present results strongly indicate that the electrode's structural stability is the key to achieving good electrochemical performance. Future work will focus on uniform distribution of Si particles in the porous carbon framework. The pore size and pore size distribution of the carbon framework will also be studied. Finally, the carbonization technique, including the types of polymer precursor, carbonization stages, and temperatures, will be optimized.

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