Carbon-Confined PVA-Derived Silicon/Silica/Carbon Nanofiber Composites as Anode for Lithium-Ion Batteries

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Abstract: Novel silicon/silica/carbon (Si/SiO2/C) composite nanofibers were synthesized by electrospinning and subsequent heat-treatment of a mixture of Si nanoparticles, sol-gel tetraethyl orthosilicate solution, and aqueous polyvinyl alcohol solution. These Si/SiO2/C nanofiber composites were also coated with amorphous carbon by chemical vapor deposition (CVD) technique. The CVD carbon-coated nanofiber composites formed freestanding, conductive nonwoven mats that were used directly as binder-free anodes in lithium-ion batteries. Results indicated that the SiO2 component of the composite anodes provided sufficient buffer function to accommodate the volume expansion of the Si nanoparticles and the CVD amorphous carbon coating helped maintain the Si nanoparticles within the carbon nanofiber matrix during repetitive charging and discharging processes. Electrochemical performance tests showed that the CVD carbon-coated Si/SiO2/C nanofiber composite was greater than 91% and the corresponding coulombic efficiency was 97.4% at the 50th cycle.

Electrochemical energy storage has been demonstrated as one of the most promising technologies for different applications such as grid storage, electric vehicles, and portable electronic devices. Because of their superior properties, including high energy density, good cycle life and good power performance, lithium-ion batteries are considered as the most preferred rechargeable battery technology in recent years. The development of high-capacity electrode materials for next-generation high-energy lithium-ion batteries is critically important for technological improvements on portable electronics and electric vehicles that use lithium-ion batteries as the power source.

Current commercial lithium-ion batteries use graphitic materials in the anode. However, graphitic anode materials cannot meet the capacity requirements of future portable electronics because of their low specific capacity of 372 mAh g\(^{-1}\). Lithium storage capacities of alloy-type anodes, such as silicon (Si), tin, germanium, etc., are much higher than that of commercially-used intercalation-type graphite anodes. Among all alloy-type anodes, Si has the highest theoretical capacity of 4200 mAh g\(^{-1}\), making it the best candidate for next-generation high-energy lithium-ion batteries. However, the insertion of lithium ions into Si during cycling induces large volumetric change (up to 400%), which causes intense pulverization of active Si material, loss of electrical contact between Si and carbon conductor, and unstable solid electrolyte interphase (SEI) formation on the Si surface. These drawbacks bring together the performance degradation of active Si material during repetitive lithiation and de-lithiation processes.

To eliminate the aforementioned drawbacks, Si-based composite anodes have been widely investigated. Among them, Si/graphite (Si/C) composites have drawn great attention, which can potentially combine the advantageous properties of Si (high capacity) and C (excellent electronic conductivity and structural stability). Maintaining the structural integrity of the electrode despite the 400% volume expansion of Si and stabilizing the SEI structure during cycling processes are, hence, the most crucial challenges for the development of Si/C based anodes. So far, there are several novel strategies for preserving the structural integrity of Si/C anode materials. One of them is to reduce the size of Si particles into nanoscale range to minimize the cracking and pulverization of these particles. Another strategy is to create open spaces between active Si particles and carbon matrix to accommodate the volume expansions of Si during cycling.

In this study, two different Si/C based anodes were synthesized: Si/SiO2/C nanofiber composite and chemical vapor deposition (CVD) carbon-coated Si/SiO2/C nanofiber composite. The fabrication approach of these two composites is schematically illustrated in Figure 1. The Si/SiO2/C nanofiber composite was first produced by electrospinning of a mixture of silicon nanoparticles, sol-gel tetraethyl orthosilicate (TEOS) solution, and aqueous PVA solution. TEOS is a common precursor for making SiO2 material while PVA is a promising candidate to produce electrospun carbon nanofibers because of its environmentally friendliness feature. After electrospinning, the resultant SiO2/PVA nanofiber composites were carbonized to obtain SiO2/C nanofibers, which formed freestanding conductive nonwoven mats and were used directly as binder-free anodes for lithium-ion batteries. Si/SiO2/C nanofibers were also coated with nanoscale amorphous carbon layer by CVD technique to ensure maintaining of the Si nanoparticles within the carbon nanofiber matrix during repetitive charging and discharging processes. Electrochemical performance tests showed that among all nanofibers studied, CVD carbon-coated Si/SiO2/C nanofiber composites exhibited the highest capacity retention of 91% and largest coulombic efficiency of 97.4% at the 50th cycle.

Experimental

Nanofiber preparation.— TEOS (99%), PVA (M\(_w\) = 85,000–124,000 g/mol, 88% hydrolyzed), ethanol, hydrochloric acid (HCl, 37%), and N,N-dimethylformamide (DMF) were supplied from Sigma-Aldrich. Si nanoparticles (diameter: 30–50 nm) were obtained from Nanostructures & Amorphous Materials, Incorporated. Deionized water was used throughout the experiments. All chemicals were used without further purification.

PVA solution (5 wt%) was prepared by dissolving PVA in ethanol, followed by adding deionized water and HCl, respectively. The molar ratio of the TEOS solution was TEOS:water:ethanol:HCl = 1:3:8:0.04. The TEOS solution was stirred at room temperature for 3 h and then gradually added to the PVA solution, followed by stirring for additional 3 h.

Nanofibers were fabricated using a standard electrospinning setup. The solution was dripped onto an aluminum foil collector at a flow rate of 1 ml h\(^{-1}\) with a syringe pump. The electrospinning conditions were as follows: applied voltage of 20 kV, nozzle-to-collector distance of 15 cm, and spinning speed of 20 mm s\(^{-1}\).

The Si nanoparticle suspension was synthesized by hydrolysis of TEOS in ethanol, followed by adding deionized water and HCl. The molar ratio of the TEOS solution was Si:TEOS:water:HCl = 1:3:8:0.04. The TEOS solution was stirred at room temperature for 3 h and then gradually added to the PVA solution, followed by stirring for additional 3 h.


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nanoparticles (17 wt% with respect to PVA) were added into the as-prepared TEOS/PVA solution and stirred at room temperature for 24 h, followed by ultrasonic treatment for 1 h to obtain a homogenous dispersion. The as-prepared Si/SiO2/PVA dispersion was then electrospun into nanofibers with a flow rate of 0.80 ml/h, a voltage of 18 kV, and a tip-to-collector distance of 25 cm. Electrospun nanofibers was stabilized in air environment at 280 °C for 5.5 h with a heating rate of 5 °C min⁻¹ and then carbonized at 700 °C for 2 h in argon atmosphere with a heating rate of 2 °C min⁻¹, during which PVA was pyrolyzed to carbon. The Si/SiO2/C nanofiber composite was further coated with amorphous carbon by the CVD method using acetylene (C2H2) as the carbon precursor gas. CVD carbon coating was applied at 700 °C for 1 h with 600 sccm flow rate of acetylene while the system was settled at 20 torr. For comparison, Si/C nanofibers were also prepared using the same electrospinning and thermal treatment procedures from a Si/PVA solution (17 wt% with respect to PVA) without the addition of TEOS.

Structure characterization.— The morphology of composite nanofibers was examined by field emission scanning electron microscope (FE-SEM, JEOL 6400F) and transmission electron microscope (TEM, JEOL JEM-2000FX). The structure of composite nanofibers was investigated by Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 470), wide angle X-ray diffraction (W AXD, Rigaku Smartlab), and Renishaw Raman microscope.

Electrochemical evaluation.— The electrochemical properties of composite nanofibers were tested using CR 2032-type coin cells. These composite nanofibers formed freestanding, conductive nonwoven mats that were used directly as the working electrode without adding polymer binder or conductive agent. Lithium ribbon (99.9%, Aldrich) was used as the counter electrode and Celgard 2400 membrane was used as the separator. The electrolyte consisted of a 1 M solution of LiPF₆ dissolved in ethylene carbonate (EC)+dimethyl carbonate (DMC)+diethyl carbonate (DEC) (1:1:1 by volume, MTI Corporation). Coin cells were assembled in a high-purity argon-filled glove box. The electrochemical performance was investigated by carrying out galvanostatic charge-discharge experiments at a constant current density of 100 mA g⁻¹ (around C/10) with cutoff potentials between of 0.01 and 2.00 V on a LAND-CT 2001A battery test system.

## Results and Discussion

Morphology and structure.— Figure 1 shows schematic illustration of the fabrication process of Si/SiO2/PVA nanofibers, Si/SiO2/C nanofibers, and CVD carbon-coated Si/SiO2/C nanofibers. The fabrication process of nanofiber electrodes consisted of three simple steps: electrospinning of Si/PVA/TEOS solution into Si/SiO2/PVA nanofibers, carbonization of electrospun nanofibers to obtain Si/SiO2/C composite nanofiber, and CVD carbon coating of Si/SiO2/C nanofibers. It was found that without the presence of SiO2, PVA-derived carbon nanofibers and Si/C nanofibers did not form freestanding mats. On the other hand, after the induction of SiO2, the resultant Si/SiO2/C nanofibers and Si/SiO2/C nanofibers formed freestanding and stable mat structure.

Figure 2 shows the FTIR spectra of PVA nanofibers, SiO2/PVA nanofibers, Si/SiO2/PVA nanofibers, Si/SiO2/C nanofibers, and CVD carbon-coated Si/SiO2/C nanofibers. PVA nanofibers showed the
peaks at 3320 cm$^{-1}$, 2920 cm$^{-1}$, 1740 cm$^{-1}$ and 1310 cm$^{-1}$, respectively, corresponding to –OH stretching, –CH stretching, –C=O stretching and scissoring vibration of –CH$_2$. The peaks at 1080 cm$^{-1}$ and 836 cm$^{-1}$ were attributed to the C–O–H stretching movement in aliphatic alcohols and out-of-plane vibration of –CH. For SiO$_2$/PVA nanofibers, the peak at 1060 cm$^{-1}$ was attributed to asymmetric Si–O–Si stretching motion and the band at 930–950 cm$^{-1}$ was attributed to Si–OH. The presence of Si–O–Si in the SiO$_2$/PVA nanofibers demonstrates the formation of the silica network in the electrospun composite nanofibers. When SiO$_2$ was formed in the PVA matrix, the –OH stretching peak of PVA at around 3300 cm$^{-1}$ was reduced, which could be explained by the intermolecular interaction between the –OH groups of PVA and silica. In addition, the broad Si–O–Si peak around 1100 cm$^{-1}$ contained a shoulder at around 1200 cm$^{-1}$, which could be attributed to the reaction between –OH groups of PVA and silanol groups of silica. The formation of this new bond and the reduction of –OH bond intensity demonstrated that silica crosslinked with PVA and formed a network structure containing Si–O–PVA–O–Si bridges (Figure 3). This network structure helped maintain the structure integrity of the nanofibers during carbonization and led to the formation of freestanding, stable SiO$_2$/C nanofiber mats. From Figure 2, it is also seen that Si/SiO$_2$/PVA nanofibers also had a characteristic SiO$_2$ peak at around 1100 cm$^{-1}$, corresponding to the symmetric stretching, asymmetrical stretching, and bending vibrations in Si-O-Si bonds. Therefore, the Si-O-PVA-O-Si containing network structure was also formed in Si/SiO$_2$/C nanofibers, leading to the formation of freestanding SiO$_2$/C nanofiber mats after carbonization. In the FTIR spectra of Si/SiO$_2$/C nanofibers and CVD carbon-coated Si/SiO$_2$/C nanofibers, the peaks around 1100 cm$^{-1}$ (asymmetry Si-O-Si bond stretching and O-Si-O bond deformation) were attributed to the SiO$_2$ ingredient in the carbonized nanofibers. The high intensities of observed characteristic SiO$_2$ peak of Si/SiO$_2$/C nanofibers and CVD carbon-coated Si/SiO$_2$/C nanofibers indicated the preserving of the SiO$_2$ structure during the carbonization and subsequent CVD carbon coating processes.

The morphology of Si/SiO$_2$/PVA nanofibers, Si/SiO$_2$/C nanofibers and CVD carbon-coated Si/SiO$_2$/C nanofibers was examined by SEM, and the results are shown in Figure 4. Continuous nanofibers with agglomerated nanoparticles and/or clusters were observed from the SEM image of electrospun Si/SiO$_2$/PVA nanofibers (Figure 4A). From Figures 4B and 4C, it was seen that the surface morphologies of Si/SiO$_2$/C nanofibers and CVD carbon-coated Si/SiO$_2$/C nanofibers were similar. Si nanoparticles were agglomerated on the nanofiber surfaces. From the TEM image of CVD carbon-coated Si/SiO$_2$/C nanofibers, the amorphous CVD carbon coating layers were not apparent. To clearly observe the thin amorphous CVD carbon layers, TEM observation was carried out, as discussed below.

Figure 5 shows TEM images of a Si/SiO$_2$/C nanofiber and a CVD carbon-coated Si/SiO$_2$/C nanofiber. For comparison, the TEM image of a carbonized SiO$_2$/C nanofiber without any Si nanoparticles is also shown. From Figure 5A, it is seen that SiO$_2$ clusters were formed along the longitudinal direction of the SiO$_2$/C nanofiber. The introduction of Si nanoparticles changed the morphology of nanofiber composites. As shown in Figures 5B and 5C, most Si nanoparticles were confined in the nanofiber matrix with some nanoparticles were agglomerated and located on nanofiber surfaces, which agree with the SEM observation in Figure 4. High-magnification TEM image is shown in Figure 5D to illustrate the CVD amorphous coating layer on a CVD carbon-coated Si/SiO$_2$/C nanofiber. It is seen that the surface of the
CVD carbon-coated Si/SiO₂/C nanofiber was coated with an amorphous carbon layer of around 15 nm thick. The nanoscale carbon coating layer is important for stable SEI formation on the active material surface during the repetitive electrochemical reactions.

The X-ray diffraction (XRD) patterns of Si/SiO₂/C nanofibers and CVD carbon-coated Si/SiO₂/C nanofibers are shown in Figure 6. For these nanofiber composites, similar diffraction peaks were indexed. Diffraction peaks at 2θ of about 29°, 47°, 56°, 69°, 76°, and 88° represent the (111), (220), (311), (400), (331), and (422) planes of Si crystals in carbon nanofiber composites, respectively. SiO₂ peaks were not detected by XRD probably due to the amorphous nature of the as-prepared SiO₂ structure. The broad and weak diffraction peak at around 2θ = 25° could be indexed as the (002) planes of disordered carbon structure, indicating the amorphous nature of the carbon nanofiber matrix and CVD carbon coating.

The structural evolution of the nanofiber composites was also investigated by Raman spectroscopy. Figure 7 shows the Raman spectra of Si/SiO₂/C nanofibers and CVD carbon-coated Si/SiO₂/C nanofibers. For these nanofiber composites, the characteristic carbon peaks of D-band (1360 cm⁻¹), representing the disordered sp² phase, and G-band (1582 cm⁻¹), indicating the in-plane stretching vibration.

Figure 5. TEM images of SiO₂/C nanofibers (A), Si/SiO₂/C nanofibers (B), CVD carbon-coated Si/SiO₂/C nanofibers (C), and high-magnification TEM image of CVD carbon-coated Si/C nanofibers (D).

Figure 6. WAXD patterns of Si/SiO₂/C nanofibers (1) and CVD carbon-coated Si/SiO₂/C nanofibers (2).
mode of E2g graphite, were observed. The relative intensity ratio (i.e., R-value) of D-band to G-band represents the degree of disorder in the structure. Typically, a higher R-value indicates a higher degree of disorder within the carbon structure. As shown in Figure 7, the R-values of Si/SiO2/C nanofibers and CVD carbon-coated Si/SiO2/C nanofibers were 0.66 and 0.77, respectively. This indicates that the carbon layer coated by CVD method is more disordered than the carbon nanofiber matrix. From Figure 7, it is also seen that due to the presence of Si nanoparticles, these nanofiber composites exhibited a Si peak at around 522 cm\(^{-1}\), which is a position for the transverse optical phonon. Si/SiO2/C and CVD carbon-coated Si/SiO2/C nanofibers also had a broad and weak peak at around 900 cm\(^{-1}\), representing the SiO2 component.

**Electrochemical performance.**— In order to evaluate the electrochemical performance of the nanofiber composite anodes, galvanostatic charge-discharge tests were conducted between 0.01 and 2.0 V at a constant current density of 100 mA g\(^{-1}\). In this study, the lithiation process is referred to discharge while the de-lithiation process is referred to charge. Figure 8 shows the galvanostatic charge-discharge profiles for the first, second and fifth cycles of Si/SiO2/C nanofibers and CVD carbon-coated Si/SiO2/C nanofibers. For comparison, the profiles of Si/C nanofibers without the presence of SiO2 are also shown. At the first cycle, the discharge capacities were 2518, 1275, and 1059 mAh g\(^{-1}\), respectively, for carbonized Si/C nanofibers, Si/SiO2/C nanofibers, and CVD carbon-coated Si/SiO2/C nanofibers. Because Si/C nanofibers were composed of only active Si and C without the inactive SiO2 ingredient, the first cycle discharge capacity of Si/C nanofibers was much higher than those of Si/SiO2/C nanofibers and CVD carbon-coated Si/SiO2/C nanofibers. However, the capacity of Si/C nanofibers decreased dramatically (from 2518 mAh g\(^{-1}\) to 652 mAh g\(^{-1}\)) at the second cycle. On the other hand, Si/SiO2/C nanofibers and CVD carbon-coated Si/SiO2/C nanofibers showed much lower capacity losses after the first charging process. From Figure 8, it was also seen that at the first cycle, Si/SiO2/C nanofibers exhibited a long voltage plateau at around 0.2 V; however, this voltage plateau was shortened after CVD carbon coating. The voltage plateau at around 0.2 V could be attributed to the alloying reaction of lithium with silicon particles exposed to the SiO2/C nanofiber surface. From Figure 8, it is also seen that the charge capacities of Si/SiO2/C nanofibers and CVD carbon-coated Si/SiO2/C nanofibers increased in the second and fifth cycles. The cycling performance and coulombic efficiencies of Si/C nanofibers, Si/SiO2/C nanofibers, and CVD carbon-coated Si/SiO2/C nanofibers are shown in Figure 9. For Si/C nanofibers, the capacity retention and coulombic efficiency at the 50th cycle were around 47% and 98%, respectively. Because of the intense capacity loss after the first discharge process, the capacity of Si/C nanofibers was much lower than those of Si/SiO2/C nanofibers and CVD carbon-coated Si/SiO2/C nanofibers. For Si/SiO2/C nanofibers, relatively stable cycling was achieved without dramatic capacity loss. At the 50th cycle, the capacity retention and coulombic efficiency of Si/SiO2/C nanofibers were around 80% and 96%, respectively. Introduction of SiO2 led to improvement in the cycling performance. This result could be attributed to the stable SiO2/C network structure because the amorphous SiO2 within the composite nanofiber structure reduced to Li2O and Li4SiO4 in the initial lithiation process, which could help buffer the volume change caused by the alloying of Si nanoparticles with Li.
Figure 9. Cycling performance (A) and coulombic efficiencies (B) of Si/C nanofibers, Si/SiO2/C nanofibers, and CVD carbon-coated Si/SiO2/C nanofibers.

and thereby increasing the cycling stability by minimizing the pulverization of the active Si material and the loss of electrical contact between Si nanoparticles and the carbon nanofiber matrix.32,42

From Figure 9, it was also seen that the cycling performance of CVD carbon-coated Si/SiO2/C nanofibers was even better than that of Si/SiO2/C nanofibers. The capacity retention and coulombic efficiency of CVD carbon-coated Si/SiO2/C nanofibers was 91% and 97.4%, respectively, at the 50th cycle. The improved cycling performance was caused by the formation of CVD carbon coating, which confined the Si nanoparticles exposed on nanofiber surfaces and helped maintain the structural integrity of the electrode during the cycling process. On the other hand, the capacity of CVD carbon-coated Si/SiO2/C nanofibers increased initially and then started to decrease. Similar capacity trend has been observed by other researchers for different carbon-confined Si/C structure materials,1,7,17 but few of them have pointed out the reason for the capacity increase during cycling. This unique behavior of CVD carbon-coated Si/SiO2/C nanofibers could be explained by the carbon confinement of the agglomerated Si nanoparticles, which were mostly located on the nanofibers surfaces. Because of the large volume expansion during the lithiation process, Si nanoparticles underwent intense pulverization, but the pulverized Si particles were confined within CVD-carbon. Due to their smaller particle sizes, these pulverized Si particles would provide shorter lithium transfer distance and facilitate more active Si for lithium insertion, leading to increased capacity for CVD carbon-coated Si/SiO2/C nanofibers. However, more work is needed to confirm this possible mechanism.

Among all three carbonized nanofibers, CVD carbon-coated Si/SiO2/C nanofibers had the best cycling performance. The rate capability of CVD carbon-coated Si/SiO2/C nanofibers was examined under different current densities (Figure 10). The highest charge capacity values under 100, 200, 400, and 800 mA g\(^{-1}\) were around 920, 820, 730, and 580 mAh g\(^{-1}\), respectively. The coulombic efficiency remained relatively constant as the current density increased. After repeated cycles at higher current densities, the charge capacity values returned to 860 mAh g\(^{-1}\) when the current density was changed back to 100 mA g\(^{-1}\). This charge capacity (860 mAh g\(^{-1}\)) was very close to initial charge capacity, indicating the good rate capability of CVD carbon-coated Si/SiO2/C nanofibers.

Figure 10. Rate capability of CVD carbon-coated Si/SiO2/C nanofibers cycled at different current densities.

Conclusions

Novel Si/SiO2/C nanofiber composite anode materials were developed for lithium-ion batteries by the combination of Si nanoparticles, sol-gel TEOS solution, and aqueous PVA solution through simple electrospinning and subsequent heat-treatment processes. To achieve good cycling performance, CVD amorphous carbon coating was applied onto Si/SiO2/C nanofibers. It was found that the SiO2 component of the nanofiber composites provided sufficient buffering function to accommodate the volume expansion of the Si nanoparticles during the repeated charging and discharging cycles. The CVD amorphous carbon coating helped maintain the Si nanoparticles within the nanofiber structure, resulting in improved cycling performance. Electrochemical performance results showed that among the composite anodes studied, CVD carbon-coated Si/SiO2/C nanofiber composites exhibited the best performance with large capacity retention of 91% and high coulombic efficiency of 97.4% at the 50th cycle. This demonstrated that CVD carbon-coated Si/SiO2/C nanofiber composites are promising anode material candidate for next-generation, high-energy lithium-ion batteries.

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