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Towards Scalable Binderless Electrodes: Carbon Coated Silicon Nanofiber Paper via Mg Reduction of Electrospun SiO₂ Nanofibers

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The need for more energy dense and scalable Li-ion battery electrodes has become increasingly pressing with the ushering in of more powerful portable electronics and electric vehicles (EVs) requiring substantially longer range capabilities. Herein, we report on the first synthesis of nano-silicon paper electrodes synthesized via magnesiothermic reduction of electrospun SiO₂ nanofiber paper produced by an *in situ* acid catalyzed polymerization of tetraethyl orthosilicate (TEOS) in-flight. Free-standing carbon-coated Si nanofiber binderless electrodes produce a capacity of 802 mAh g⁻¹ after 659 cycles with a Coulombic efficiency of 99.9%, which outperforms conventionally used slurry-prepared graphite anodes by over two times on an active material basis. Silicon nanofiber paper anodes offer a completely binder-free and Cu current collector-free approach to electrode fabrication with a silicon weight percent in excess of 80%. The absence of conductive powder additives, metallic current collectors, and polymer binders in addition to the high weight percent silicon all contribute to significantly increasing capacity at the cell level.

Silicon is widely considered as the successor to graphite-based anodes for Li-ion batteries given its highest theoretical capacity among known materials of 3579 mAh g⁻¹, which corresponds to an ambient temperature formation of Li₁₅Si₄¹. The large amount of attention garnered by Si as an anode material is also due to its high abundance as a rock-forming element, non-toxicity, and environmental benignity². Silicon's ability to alloy with large amounts of Li leads to volume expansion in excess of 300%, which can pulverize active material, deteriorate electrical connectivity, and degrade the solid electrolyte interphase (SEI) layer³. These phenomena can drastically reduce the cycle life and capacity of Si-based anodes. Si can fracture upon lithiation when the characteristic dimension is as small as 150 nm^{4–6}. Scaling of Si nanostructures below this critical dimension affords avoidance of active material fracture and pulverization. However, expansion and contraction of Si during cycling may lead to repeated fracturing and reformation of the SEI layer⁷. Numerous nanostructures such as porous Si nanowires, double walled Si nanotubes, and porous Si nanoparticles (SiNPs) have all demonstrated effective preservation of the crucial SEI layer via control of the volume expansion of Si^{7–9}.

Si also suffers from low electrical conductivity, thus it is used in conjunction with conductive matrices such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), or conformal carbon coatings^{10,11}. Electrospinning has been extensively used to produce carbonaceous nanofibrous matrices of wide ranges of composition for applications in energy storage. Traditionally, polymers dissolved in organic solvents along with dispersed active material, such as Si or Fe₂O₃, are electrospun to produce polymer fibers with embedded nanoparticles^{12,13}. However, these organic polymer-based fibers can require lengthy thermal oxidative stabilization (TOS) and carbonization steps for applications in energy storage devices¹⁴. Additionally, the final weight percent of active material in the fibers can be much less than 50% which significantly reduces the total electrode capacity¹⁵. A majority of the weight of the fibers corresponds to the conductive carbon matrix, which stores much less Li than the embedded active materials¹⁶.

Li metal has garnered attention as a potential anode material for Li-S and Li-ion batteries based on its theoretical capacity of 3860 mAh g⁻¹, high conductivity as a metal, low density (0.59 g cm⁻³), lowest negative

electrochemical potential (-3.040 V vs. the standard hydrogen electrode), and lack of intercalation or diffusion of Li-ions as is required in Si-based and C-based anodes^{17,18}. The two most significant barriers to commercialization of these Li-metal anodes is the phenomena of Li dendrite growth and relatively low Coulombic efficiency (CE) via repeated consumption of Li and electrolyte. The formation of Li dendrites poses serious safety hazards due to the potential of short circuits and high surface area with repeated cycling. Despite surface treatments and the use of various electrolytes, the challenges of preventing Li dendrite growth and increasing the relatively low CE to $>99.9\%$ still require significant work to overcome^{19–22}.

In industrial settings, battery electrodes are produced via the decades-old slurry method in which metallic current collectors are coated with a slurry comprising an inactive polymer binder, carbon black, and active material dispersed in an organic solvent (usually NMP). However, the necessity of these metal current collectors and inactive polymer binders adds significant cost and weight to the final battery assembly, especially in large battery banks used in EVs. In order for a leap in full cell capacity to occur, significant changes in the way electrodes are manufactured must take place in addition to the introduction of high capacity materials such as Si. Herein, we report on the first synthesis of a binderless free-standing Si nanofiber (SiNF) paper with a Si weight percent in excess of 80% for application as Li-ion battery anodes, which forgoes the need for inactive polymer binders or metallic current collectors.

Results

SiNF paper is synthesized via magnesiothermic reduction of electrospun SiO_2 nanofiber (SiO_2 NF) paper, which is produced by an *in situ* acid-catalyzed polymerization of TEOS in-flight. Two solutions comprising TEOS:EtOH 1:2 (mol:mol) and H_2O :HCl 200:1 (mol:mol) are prepared separately under vigorous stirring. The H_2O :HCl solution is then added drop-wise into the TEOS:EtOH solution under stirring to produce a sol with a 1:1 EtOH:H $_2\text{O}$ molar ratio. The sol is aged at 70°C for 2 hours, loaded into a polypropylene syringe, and connected to an Invenso Nanospinner Ne300 multi-nozzle electrospinner. The tip-to-collector distance was held constant at 12 cm and the applied voltage was 30 kV. The spinning process can be visualized in Fig. 1a. During electrospinning, the sol is drawn from the Taylor cone and the TEOS undergoes *in situ* polymerization in-flight to produce SiO_2 NFs on the collector plate. The white SiO_2 NF paper, as in Fig. 1b, is easily removed from the collector plate by hand and can be facily handled and cut to desired

geometries. Relatively lengthy spinning times (1–3h) resulted in NF paper several millimetres thick while shorter times ($<1\text{h}$) resulted in thin, highly flexible translucent sheets. Production of SiO_2 NF paper reached several grams per hour depending on the number of nozzles used and flow rate, which demonstrates the excellent scalability of producing the precursor to the SiNF paper.

After electrospinning, the SiO_2 NF paper sheets were dried at 200°C under vacuum for 1 hour to remove residual H_2O and EtOH and to ensure the full polymerization of all NFs. Noticeable shrinkage was observed in the NF paper, suggesting a partially incomplete polymerization or residual amounts of H_2O and EtOH within the NFs. However, the paper retains its original shape and ease of handling after drying, and no cracking or warping was observed in the sheets.

SEM imaging in Fig. 2a and 2b shows the morphology of as-spun SiO_2 NFs. XRD data in Fig. 2e reveals the amorphous nature of the as-spun SiO_2 NFs. There is no evidence of nanoparticle-like SiO_2 structures, which are commonly produced via the Stöber method; instead, the SiO_2 NFs are an amorphous, solid network of silica²³. SiO_2 NF paper is then cut into strips and loaded into steel-capped brass union Swagelok reactors with -50 mesh Mg powder in a SiO_2 :Mg weight ratio of 1:1. The reactors are sealed in an Ar-filled glovebox (0.05 ppm O_2) and immediately transferred to an MTI GSL1600X quartz tube furnace. The furnace is purged with Ar and heated at $5^\circ\text{C}/\text{min}$ to 700°C and held for 2 hours to ensure complete reaction of Mg and SiO_2 . A 2 hour reduction corresponds to a yield of 43.2%, which is very near the theoretical yield of Si from SiO_2 (46.7%), as in Fig. 3a. Beyond this time only marginal gains in yield are achieved, thus it is not necessary to reduce for longer periods of time. Yield data was calculated by measuring the weight of the etched SiNF paper in comparison to the weight of the original SiO_2 NF paper. XRD data in Fig. 2e reveals the existence of both MgO and Si, as expected, in the as-reduced SiNF paper. The reduced NF paper is submerged in 2 M HCl for 3 hours to remove the reaction products MgO and possibly Mg_2Si . No evidence of SiH_4 was observed, suggesting minimal or no Mg_2Si was formed. Etched SiNF paper assumes a brownish-yellow color as in Fig. 1c. After rinsing the SiNF paper several times in EtOH and H_2O , the sheets are dried under vacuum at 105°C overnight. SiNF paper after etching can be seen in the SEM images in Fig. 2c and 2d. In contrast to the solid SiO_2 NFs, SiNFs have a noticeable porosity that exists throughout the diameter of the fiber, as evidenced in the fractured SiNF in Fig. 2d. This porosity is derived from the selective etching of MgO and pos-

Figure 1 | (a) Schematic representation of the electrospinning process and subsequent reduction process. Digital photographs of (b) as-spun SiO_2 NF paper, (c) etched SiNF paper, and (d) C-coated SiNF paper as used in the Li-ion half-cell configuration.

Figure 2 | SEM images of (a) SiO₂ NFs after drying, (b) SiO₂ NFs under high magnification (c) SiNFs after etching, and (d) SiNFs under high magnification. (e) XRD analysis of NFs at select synthesis steps.

sibly Mg₂Si sites. XRD data in Fig. 2e reveals the existence of crystalline Si after etching of reaction products. Brunauer-Emmett-Teller (BET) surface area measurements in Fig. 3b confirm the existence of a large population of mesopores centered around ~10 nm and a relatively high surface area of 281 m²g⁻¹. The pore distribution is in good agreement with the TEM images in Fig. 4.

Figure 3 | (a) Yield data for SiNF paper as a function of reduction time. (b) BET surface area measurements of SiNF paper with type IV N₂ sorption isotherms and inset showing the distribution of pore diameters.

TEM imaging in Fig. 4 reveals the morphology of the fibers before and after Mg reduction. No porosity is observed in the SiO₂ NFs, as in Fig. 4a, which reveals a uniform solid fiber. After reduction and etching the SiNFs assume a highly porous morphology as evidenced in Fig. 4b and 4c. This porous structure is present throughout the thickness of the fibers, which was previously observed in the SEM images in Fig. 2d and 2e. The HRTEM image in Fig. 4d reveals the presence of not only silicon nanoparticles (SiNPs) but also the existence of a native SiO₂ shell on all SiNPs with a thickness of 1–2 nm. The SiO₂ shell may not only serve to mitigate volume expansion effects experienced by the SiNPs during lithiation, but it is also a lithiatable shell with a theoretical reversible capacity of 1961 mAh g⁻¹^{24,25}. The diameter of the interconnected SiNPs that comprise the SiNFs are 8–25 nm, which is well below the critical size for the fracture of Si during lithiation. The small size of the SiNPs also reduces the bulk diffusion length for Li into Si.

Due to silicon's low conductivity, we applied a ~4 nm carbon coating to all SiNF paper electrodes to enhance the surface conductivity of the electrodes. The carbon coating process was proven in our previous work and the effects of the thickness or crystallinity of the carbon coating on performance are beyond the immediate scope of this investigation²⁶. The advantages and limitations of a carbon coating have been extensively studied in both anode and cathode settings^{27–29}. SiNF paper was loaded into a quartz tube furnace in a quartz boat and heated to 950°C in 15 minutes under a flow of Ar:H₂ at 700 torr. At 950°C, C₂H₂ was introduced for 15 minutes and then the system was cooled to room temperature under flow of Ar:H₂. The C-coated electrodes assume a black color as in Fig. 1d. Weighing after C-coating reveals a carbon content of ~18.5% with the remainder corresponding to Si. C-coated SiNF paper electrodes were used as-is without the addition of acetylene black or a binder and were cut down to fit inside of 2032-type coin cells. Li metal was used as the counterelectrode with a 1:1 EC:DMC (v:v) electrolyte with a 3% vol. VC additive for improved cycle life, and Celgard PP was used for the separators. Charge-discharge cycling was performed on an Arbin BT300 and cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on a Biologic VMP3. All capacity values were calculated on the total electrode weight (carbon + silicon).

Discussion

Charge-discharge cycling in Fig. 5a reveals the excellent performance of the C-coated SiNF electrodes over 659 cycles, with minimal

Figure 4 | TEM images of (a) SiO₂ NF after drying, (b) SiNF after etching, (c) SiNF after etching showing porosity, (d) HRTEM image of SiNF showing 3.14 Å lattice spacing of Si(111).

capacity fading after the first 20 cycles. Even after 659 cycles, the SiNF electrodes can deliver a reversible capacity of 802 mAh g⁻¹ with a Coulombic efficiency of 99.9%. We attribute this excellent stability to the internal porosity of the SiNFs, which allows for internal volume expansion of the small SiNPs. This internal expansion of Si within the SiNFs effectively preserves the crucial SEI layer that coats the outside of the SiNFs. The existence of the native oxide shell and C-coating also contribute to mitigating volume expansion related effects through creation of a buffer layer. For comparison, cycling data for bare uncoated SiNFs is presented in Fig. 5a to emphasize the importance of the C-coating process. The capacity rapidly decays below the theoretical capacity of graphite within 100 cycles when no coating is present.

CV measurements in Fig. 5b demonstrate the activation process of the electrodes over the first 20 cycles. The 19th and 20th cycle curves largely coincide with each other, which signals the stabilization of the electrode. This activation process may be due to the gradual lithiation of the native SiO₂ shell and SiNPs located in the interior regions of the NFs³⁰. The peak associated with the formation of SEI occurs at 0.67 V and is non-existent in subsequent cycles. Peaks closely associated with the dealloying (0.51 V and 0.37 V) and alloying (0.18 V) of Si sharpen with increased cycling, confirming the existence of the activation process. After activation for 20 cycles to allow for capacity stabilization, C-rate testing was performed on C-coated SiNFs, as in Fig. 5d. Even up to the C/5 rate, C-coated SiNFs outperform the theoretical capacity of graphite.

The 1st cycle is performed at C/40 and the 2nd at C/20 in order to allow for activation of a majority of the active material while fostering the formation of a well-structured SEI. The capacity of our SiNF paper anode is slightly lower compared to other published silicon anodes on a pure active material basis due to the thick nature of the electrodes and large diameter of some NFs. However our SiNF paper electrodes have the remarkable benefit of having no metallic current collectors or polymer binders. When the copper foil weight is taken

into account in the slurry-based electrodes, the capacity is significantly lower than reported. Additionally, all of our capacity values are reported on a total electrode weight basis, unlike much of the reported values in literature which exclude weight contributions of carbon additives, binders, or current collectors. In this sense, our SiNF electrodes outperform the slurry-based electrodes if the weight of the copper foil is taken into account. The SiNF paper has a loading of Si in excess of 80% by weight and is a completely binder-free approach. SiNF paper electrodes demonstrate excellent Coulombic efficiencies between 99–100% after the first three cycles. Charge-discharge curves in Fig. 5c are in good agreement with the CV curves and demonstrate the low discharge potential of the SiNF electrodes. EIS measurements in Fig. 5e also coincide with the activation process of the electrodes during initial cycling.

To prove the superiority of our free-standing C-coated SiNF anodes to that of other electrospun slurry-cast anodes in terms of gravimetric capacity, we provide the following example. Jeong *et al.* recently synthesized a core-shell structured SiNPs@TiO_{2-x}/carbon composite Li-ion anode material via electrospinning³¹. However, the long-range 3D nanofiber network produced during electrospinning is destroyed via turning the fibers into a powder which is then cast in the traditional slurry cast method onto Cu foil. A 12 mm diameter Cu current collector disk with a thickness of 10 μm corresponds to a weight of 10.133 mg. Additionally, carbon black and an inactive polymer binder were added which constitute 10 wt.% each of the electrode. Their reported capacity of 939 mAh g⁻¹ is solely based on the active material weight and excludes the weight contributions of the Cu foil, carbon black, and polymer binder. With a reported maximum loading of 3 mg of active material, this corresponds to a capacity of 2.817 mAh. Taking into account the 10 wt.% contributions of the polymer binder and carbon black (0.375 mg each), plus the 10.133 mg Cu foil, the actual capacity of the entire anode is 202.7 mAh g⁻¹. Comparing this value to that of our free-standing C-coated SiNF anodes (802 mAh g⁻¹), it is clear that our anodes can

Figure 5 | (a) Cycling data for C-coated SiNFs compared to uncoated SiNFs at C/10 ($1C = 4 \text{ A g}^{-1}$). (b) Cyclic voltammogram for select cycles for C-coated SiNFs using a scan rate of 0.05 mV s^{-1} (c) Charge-discharge curves for select cycles for C-coated SiNFs. (d) C-rate data for C-coated SiNFs at select rates. (e) PEIS curves for select cycles for C-coated SiNFs with inset showing equivalent circuit used for modelling. (f) Resistance data for select cycles for C-coated SiNFs, with inset graph displaying ESR values.

provide nearly four times the gravimetric capacity based on consideration of the weight of all anode components.

Potentiostatic EIS was used to analyze interfacial and diffusion related kinetics in the SiNF electrodes in the delithiated state. The equivalent circuit used in this work, as in Fig. 5e, contains the following major components: i) equivalent series resistance (ESR), ii) contact impedance within the active material (R_C and CPE_C), iii) impedance due to the SEI layer formation (R_{SEI} and CPE_{SEI}), iv) interfacial impedance at the surface of the NFs (R_{CT} and CPE_{DL}), and v) diffusion impedance (W_O). Constant phase elements (CPEs) are used to

describe non-ideal capacitances that arise due to non-uniformity in the size and shape of the NFs. EIS data for select initial cycles is plotted in Fig. 5e and 5f. All associated resistances tend to decrease initially and then stabilize, which coincides with the activation and stabilization of the electrode. Charge transfer resistance decreases the most drastically, with a 700% reduction from the 1st to the 11th cycle. The decrease of resistances such as ESR and R_C is a result of the electrode activation process, where the conductivity between SiNPs is enhanced. The lithiation of the native oxide shell may also enhance the conductivity between the interconnected SiNPs with cycling. The

extraordinarily low ESR of these electrodes relative to other published Si anodes is most likely due to the absence of a polymer binder and existence of very large void spaces between SiNFs, which permits relatively facile Li-ion travel. The very low charge transfer resistance can be attributed to the highly conductive C-coating.

The *in situ* polymerization of TEOS that occurs in-flight during the short travel distance of 12 cm from tip to collector plate, proceeds in the following general fashion in Eq. 1:

In contrast to the conventional Stöber method, which may take as much as 24 hours to precipitate appreciable amounts of silica NPs, our *in situ* polymerization of TEOS in-flight is comparatively instantaneous³². This may be due to the relatively high surface area for solvent evaporation afforded by the formation of a nanoscale fiber immediately proceeding the Taylor cone. The absence of silica NPs in the as-spun SiO₂ NFs also confirms this rapid polymerization of TEOS in-flight. Subsequent magnesiothermic reduction of the SiO₂ NFs proceeds as in Eq. 2 and removal of MgO proceeds as in Eq. 3:

It is worth noting that MgCl₂ can be recycled back into Mg via electrolysis, which is a common industrial route for producing Mg from brine³³. The Mg reduction route operates at a much lower operating temperature (700 °C) than carbothermal reduction, which requires electric arc furnaces operating at >2000 °C. Carbothermal reduction is the predominant method used to produce metallurgical grade Si, but it is not a carbon neutral process in itself. Conversely, Mg reduction produces a solid, environmentally benign, and recyclable MgO product at much lower operating temperatures.

In conclusion, we have successfully demonstrated the first synthesis of a scalable carbon-coated silicon nanofiber paper for next generation binderless free-standing electrodes for Li-ion batteries that will significantly increase total capacity at the cell level. The excellent electrochemical performance coupled with the high degree of scalability make this material an ideal candidate for next-generation anodes for electric vehicle applications. C-coated SiNF paper electrodes offer a highly feasible alternative to the traditional slurry-based approach to Li-ion battery electrodes through the elimination of carbon black, polymer binders, and metallic current collectors.

Methods

SiO₂ NF Synthesis. Two solutions comprising TEOS:EtOH 1:2 (mol:mol) and H₂O:HCl 200:1 (mol:mol) are prepared separately under vigorous stirring. The H₂O:HCl solution is then added drop-wise into the TEOS:EtOH solution under stirring to produce a sol with a 1:1 EtOH:H₂O molar ratio. The sol is aged at 70 °C for 2 hours, loaded into a polypropylene syringe, and connected to an Invenso Nanospinner Ne300 multinozzle electrospinner. The tip-to-collector distance was held constant at 12 cm and the applied voltage was 30 kV. The SiO₂ NF paper sheets were removed from the collector, placed in a vacuum oven at 200 °C, and dried overnight under vacuum.

C-coated SiNF Synthesis. SiO₂ NF paper is cut into strips and loaded into steel-capped brass union Swagelok reactors with -50 mesh Mg powder in a SiO₂:Mg weight ratio of 1:1. The reactors are sealed in an Ar-filled glovebox (0.05 ppm O₂) and immediately transferred to an MTI GSL1600X quartz tube furnace. The furnace is purged with Ar, heated at 5 °C/min to 700 °C, held for 2 hours, and finally cooled under forced convection to room temperature. As-reduced paper strips are submerged in 2M HCl for 3 hours to remove MgO and then rinsed several times with DI H₂O and EtOH. Etched SiNF paper strips are dried overnight under vacuum at 105 °C. SiNF paper was loaded into an MTI GSL1600X furnace in a quartz boat and heated to 950 °C in 15 minutes under a flow of 0.180 SLM Ar and 30.0 SCCM H₂ at 700 torr. At 950 °C, 30 SCCM C₂H₂ was introduced for 15 minutes and then the system was cooled to room temperature under flow of Ar:H₂.

Battery Characterization. C-coated SiNF paper was cut to fit inside 2032-type coin cells. Celgard 3501 PP was used for separators. Li metal was used as the

counterelectrode with a 1:1 EC:DMC (v:v) electrolyte with a 3% vol. VC additive for improved cycle life. Charge-discharge cycling was performed on an Arbin BT300 and cyclic voltammetry (CV) and potentiostatic electrochemical impedance spectroscopy (PEIS) measurements were performed on a Biologic VMP3. All capacity values were calculated on the total electrode weight (carbon + silicon). Capacity was determined using $1\text{C} = 4\text{ Ag}^{-1}$ and CV was performed using a scan rate of 0.05 mVs⁻¹.

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Author contributions

Z.F., M.O. and C.S.O. designed the experiments and wrote the main manuscript. Z.F., H.B., Z.M., K.A., R.L., and R.Y. conducted characterization of the material, material synthesis, and

battery fabrication and characterization. C.S.O. managed the research team. All authors reviewed the manuscript.

Additional information

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