Hierarchical Porous Framework of Si-Based Electrodes for Minimal Volumetric Expansion

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The demand for the full implementation of lithium-ion batteries (LIBs) in powering applications such as electric vehicles has promoted vast research towards new materials with higher capacities and longer lifetimes. [1] Commercialized graphite anodes stand far from achieving this goal due to their capped specific capacity of 372 mAh g$^{-1}$. The search for new anode materials capable of reversibly retaining large amounts of lithium is a necessity in creating advanced LIBs. One such material is silicon (Si), which is naturally abundant and able to form Li$_x$Si compounds, where x can reach a value of 3.75 at room temperature corresponding to a specific capacity of 3579 mAh g$^{-1}$. However, the alloying of lithium into Si leads to an increase in its specific volume of about 300%, creating a number of challenges that have retracted the implementation of Si as a LIB anode material.

Stress induced by large volume changes of the Si anodes causes material degradation and major problems for electrochemical performance. In early studies, cracking and pulverization of the Si particles was considered to be the main reason for the rapid capacity loss. [6] Recently, X. H. Liu et al. provided direct evidence that the tendency for fracture and decrepitation of the Si active material can be prevented by reducing the material size to the nanometer range. Indeed, the strain in such Si nanoparticles can be relaxed without mechanical fracture because of their small size and high surface energy resistance. [3] Consistent with X. H. Liu et al., there has been some success in addressing material stability issues by designing nanostructured Si materials including nanowires, nanotubes, nanoporous films, and Si nanoparticles/carbon composites. [4] The strategy of engineering electrode nanostructures has greatly improved some of the challenges associated with the use of Si-based electrodes. Despite these advances, the cracking and breaking of the composite electrode's microstructure, and thereby its conductive network, due to the drastic volumetric changes has become one of biggest problems in realizing an electrochemically stable and long lasting Si-based anode.

In addition to the degradation of the composite electrodes, the inherent volume change of Si also induces composite electrode thickness expansion and external cell deformation. From a practical point of view, cell deformation is as important as electrochemical performance and it is the critical factor limiting the commercialization of Si-based anode materials. [7] An acceptable degree of thickness change for the electrodes is about 10–13%, like that of commercialized graphite electrodes. [8] A few approaches have been taken to alleviate cell deformation, including control of electrode porosity [9] and the use of functional binders. [10] However, the practical level of electrode thickness confinement throughout cycling has been substandard. With a conventional polyvinylidene fluoride (PVDF) binder, Si-based electrodes usually exhibit a large change in electrode thickness over 100%. [11] Material engineering and the development of various binders have shown to reduce this conventional electrode thickness expansion to a level of about 40%. [12, 13] Q. Si et al. showed further improvement to the latter electrode deformation level with their carbon paper substrate for Si/C composite anodes, with an expansion of 20%. [14] The smallest electrode deformation after full lithiation for Si-based electrodes reported to date, was recently demonstrated by Y. Park et al. with an electrode thickness change of 18%. This small change in cell expansion was enabled by the ensemble effect of the buffering volume change of Si by voids of hollow carbon and adoption of a crosslinked CMC-PAA binder. [7] Despite such recent efforts, the synthesis of many of the materials used to mitigate cell deformation and electrode degradation is complex and costly, making the scalability for mass manufacturing extremely difficult. In this work, we present the manufacturing of a scalable and low-cost material that attains an even lower electrode deformation than that demonstrated by Y. Park et al.’s study.

In order to address the challenges that come with nano-Si based anodes' volume expansion and electrode deformation, we designed a scalable and inexpensive process to make highly reversible, low expansion, nano-Si composite electrodes by embedding Si nanoparticles in a tunable cyclized-polyacrylonitrile (cPAN) fiber network bound together by a cPAN coating. Figure 1a shows a detailed schematic of the manufacturing process of the nano-Si hierarchical porous framework electrodes that herein will be referred to as nSi@cPAN/cPAN. The electrospinning of nano-Si and PAN (Figure 1a i.) results in a fiber-mat-like material (Figure 1a ii.) that is very easy to handle despite the fact that we are dealing with nano-size Si particles. The resulting electrospun material is heat-treated to cyclize the PAN fibers (Figure 1a iii.) As shown in our previous work, the cyclization of PAN provides a mechanically resilient pyridine-based conjugated polymer that has good conductive
properties, which are essential characteristics for our hierarchical porous framework. After cyclization is complete, the nSi@cPAN fibers are dispersed into a PAN – N,N-dimethylformamide (DMF) solution (Figure 1a iv.). This allows for the utilization of PAN, once again, as a resilient coating and binder to preserve the nSi@cPAN fiber structure and create an intimately linked conductive framework. The slurry created with nSi@cPAN/PAN is directly doctor bladed onto a copper current collector and then heat-treated to cyclize the added PAN coating/binder creating the nSi@cPAN/cPAN electrodes (Figure 1a v.). The unique properties obtained from the cyclization of PAN allow for the exclusion of conductive additives and/or binders. Inspired by the properties achieved with cPAN in our previous work, this hierarchical porous framework is developed to focus on mitigating the overall deformation of the electrodes and consequently their fast degradation by providing both a robust and reversible electrode network.

The previously described fabrication process for the nSi@cPAN/cPAN anodes aims towards the conservation of the fibrous, linked, conductive electrode network. With the use of field emission scanning electron microscopy (FESEM) we confirm that our process does preserve the electrospun nSi@cPAN fibers throughout electrode manufacturing. Figure 1b and 1c show the FESEM images of the nSi@cPAN fibers as spun (step iii. – Figure 1a) and the nSi@cPAN/cPAN electrodes (step v. – Figure 1a), respectively. The fiber network’s long-term structural integrity is critical for reduced electrode deformation as well as improved and stable electrochemical performance. There has been a great deal of work done on the electrospinning of Si nanoparticles and PAN, but most previous methods carbonize PAN, creating a more brittle fibrous matrix that cannot accommodate Si’s volume changes for stable extended cycling. Previous methods also mechanically mix conductive additives (acetylene black, AB) and binders (PVDF) to the spun fibers for electrode manufacturing, breaking down their pristine fibrous structure. Our fabrication process allows us to maintain the structural integrity of the fibers without auxiliary materials, such as conductive additive and PVDF, leading to an electrode microstructure that enables a reversible high capacity nano-Si composite.

Transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) were utilized to characterize the microstructure of the nSi@cPAN/cPAN electrodes. TEM samples were prepared using a focused ion beam (FIB) equipped with a mobile air-lock chamber. Micrographs of the TEM sample preparation by Ga+ ion milling are presented in Figure S1. Figure 1 also presents TEM micrographs (Figure 1d, 1e and 1f) and EELS elemental mapping (Figure 1g) of an uncycled nSi@cPAN/cPAN electrode. We observe the nano-Si particles (red mapping) completely embedded in the cPAN fibrous network (cyan mapping). Fully embedding the nano-Si particles into the cPAN fibers provides complete protection for the nano-Si particles from direct contact with the liquid electrolyte.
keeping the nanocomposite electrode degradation and deformation to a minimum. Furthermore, the utilization of cPAN to bind the whole fibrous network creates a resilient and intimately linked conductive framework that connects all of the active material throughout the electrode. [12]

Electrochemical characterization was utilized to study the ability of the @cPAN/cPAN framework to improve the cycling performance of a high capacity material such as Si. Figure 2a presents the cyclic stability and coulombic efficiency (CE) of the nSi@cPAN/cPAN electrodes. The electrode was cycled at a rate of C/20 for the first 5 cycles and a rate of C/10 for all subsequent cycles. We observe a specific charge capacity of 788 mAh g⁻¹ and a CE of 99.5% after 20 cycles, and a specific charge capacity retention of 94.6% after 45 cycles at a rate of C/10. It should be noted that the specific capacity in this work was normalized based on the mass of the whole electrode film (nSi@cPAN/cPAN) in each cell.

As expected, we observe an increase in specific capacity of the electrodes as the voltage window is increased. Even as higher stresses are introduced by increasing the amount of Li⁺ electrochemically reduced, the electrode running to 0.005 V vs. Li/Li⁺ shows good stability rather than a fast deterioration, verifying the favorable mechanical properties of the @cPAN/cPAN framework. At cycle 20 we observe a specific charge capacity of 1161 mAh g⁻¹ and a CE of 99.7%. The voltage profiles of both cells presented here are included in Figure S2. In addition to studying the electrochemical stability limits of the nSi@cPAN/cPAN electrodes by increasing the amounts of Li⁺ alloying and dealloying during cycling, we also investigated the behavior of the manufactured anodes in a full-cell configuration. Again, we found good electrochemical stability and no mechanical issues due to electrode expansion. The details and results of the full-cell experiment are included in Figure S3.

In lieu of direct electrical conductivity measurements of the PAN framework, we used electrochemical impedance spectroscopy (EIS) to measure ohmic resistance of the nSi@cPAN/cPAN electrodes. The ohmic resistance was found to be 4.00 Ω, from which 1.02 Ω is attributed to the electrode film and the rest results from the liquid electrolyte (Figure S4). These numbers compare very similarly with our previous nano-Si cPAN work,[12] and suggests minimal electronic and ionic polarizations coming from the nSi@cPAN/cPAN electrode film. We also conducted a rate test to study the transport properties of the nSi@cPAN/cPAN electrodes (Figure 2b). At a rate of 5C, the electrode exhibits an average specific charge capacity of 526 mAh g⁻¹. The magnitude of the charge capacities at a rate of 5C suggests that the @cPAN/cPAN framework provides
adequate ionic and electronic transport. Also, after the 5C rate test was conducted, the electrodes were cycled at a rate of 0.5C and were able to completely recover their initial specific charge capacities at that rate attesting to the maintenance of the electrode’s structural integrity. At this time, a direct ionic and electronic transport mechanism for the @cPAN/cPAN has yet to be elucidated. To investigate this phenomenon, we ran an electrode in a half-cell configuration without Si active material. The electrode was comprised of only the @cPAN/cPAN framework. The results show the initial electrochemical activity of the cPAN and then subsequent reversible cycling stability in the liquid electrolyte (Figure S5). These results corroborate our previous ohmic resistance and rate test results and prove the capability of cPAN to ionically and electronically conduct after initial electrochemical activation.

In order to study the morphological properties of the @cPAN/cPAN framework and its influence on Si’s volumetric expansion, FESEM samples were prepared from composite electrodes at different stages of cycle life. Figure 3 presents FESEM micrographs of electrode cross-sections, prepared using FIB, before and after initial lithiation and then after the 20th delithiation cycle. Figure 3a shows the cross-section of the uncycled nSi@cPAN/cPAN electrode with an initial thickness of 21.66 µm. Figure 3b presents the initial lithiation of the electrode showing a minimal percent expansion of only 14.3%, nearly that of state-of-the-art graphite anode. [8] Si’s massive volumetric change of 300% is almost fully accommodated by our nano- and micron-size porous electrode framework. Even after 20 cycles of high stress and strain, the integrity of the electrode is preserved and the maximum volumetric change is only 23% relative to the uncycled state (Figure 3c). This exceptional volume control, resulting from the @cPAN/cPAN framework, is of paramount importance in the effort to not only conserve intimate particle contacts and conduction pathways throughout the electrodes but to also subside electrode deformation.

To further investigate this remarkable volume control and prove that our framework is indeed surviving the substantial strains and stresses induced by nano-Si, we looked more in-depth into the TEM micrographs and EELS mapping from each of our fully lithiated and cycled cross-sections. Figure 4 presents the TEM micrographs (Figure 4a, 4b and 4c) and EELS mapping (Figure 4d) of the fully lithiated nSi@cPAN/cPAN electrode as well as the TEM micrographs (Figure 4e, 4f and 4g) and EELS mapping (Figure 4h) of the 20th delithiated cycled electrode. The TEM and EELS of both the fully lithiated and cycled electrodes show no significant mechanical deficiencies within the electrodes’ framework. The fully lithiated nSi@cPAN/cPAN electrode exhibits the capability to house the expanded nano-Si particles with no fracture or particle/network disconnections. These observations are substantiated by observing images of the cycled electrode. At the 20th delithiation and full contraction of the nano-Si particles, the nSi@cPAN/cPAN shows no severance of connections between particles and the porous network. This intimate contact between particle and framework provides a linked conductive network that prevents the isolation of active material and enables its full utilization throughout cycling.

The favorable combination of mechanical and electrochemical properties we have presented with this work addresses many of the continuing issues that have prevented the commercialization of Si-based anodes. We have demonstrated the remarkable capability of the manufactured framework to almost fully accommodate all the volumetric changes exhibited...
by Si along with a minimal electrode deformation. The scalable and low-cost process designed here is not only a good model for highly reversible Si nanocomposite anodes, but it can be readily applied to other LIB electrode materials that suffer form volume expansion. Future work will be focused mainly on further improvement of the CE of our electrodes through surface treatments and electrolyte modification. The improvement of the CE is another very important concern for Si-based anodes and it goes hand in hand with mechanical integrity and overall volume control.

Experimental Section

Material Preparation: We use electrospinning for the production of PAN-based fibers with embedded nano-Si particles. Polyacrylonitrile (PAN, Mw = 150,000 g mol$^{-1}$) and nano-Si particles (Alfa Aesar, 50 nm) were hand mixed in a mortar and pestle (2.5:1 wt. ratios) and then dissolved in N,N-dimethylformamide (DMF, 99%). The solution was mixed via magnetic stirring for 15 hours and then injected into a 10 mL syringe and to the electrospinning nozzle. The gauge number of the needle used for the electrospinning was 18 and the flow of the solution was fixed to 0.7 mL/hr using a syringe pump. The applied voltage was 27 kV and the needle-to-collector distance used was 20 cm. After the solution was electrospun, the nSi@PAN fibers were collected and dried at 60 °C for 1 hr. The fibers were then heat treated in air at 220 °C to achieve the cyclization of PAN. The nSi@cPAN fibers were then mixed with PAN powder at 9:1 wt. ratio (fiber:PAN) in DMF via magnetic stirring for 15 hrs to produce a viscous slurry. The slurry was directly dried onto a copper foil and dried at 60 °C for 2 hrs to form an electrode film. The dried electrode was calendared and cut with a 0.5” diameter punch. Each punch went through a heat treatment under argon in a tube furnace at 300 °C for 12 hrs to cyclize the added PAN coating, thus stabilizing the electrodes as a whole. Cells were assembled in an Ar-dry box and tested at room temperature. Electrochemical measurements were all performed based on the mass of each 0.5” electrode film (typically 1.5–2.0 mg, where 26% is active Si material).

Nano-Si Material Characterization: The work presented here has followed several other studies in our group that has also utilized the same commercial nano-Si material. We have included additional characterization from previous work done with this same commercial nano-Si material. The material appended provides detailed information regarding the nano-Si material’s morphology type, size distribution, surface state, and structure.[12] This additional information, included in Figure S6, will offer the reader further clarity and a better knowledge on the commercial nano-Si material employed in this work.

Electrochemical Measurement: Electrochemical measurements were carried out using an Arbin 2000 battery test station. All cells were assembled using the prepared nSi@cPAN/cPAN coating electrodes as the working electrodes and lithium metal foil as the counter electrode. The electrolyte was 1M LiPF$_6$ dissolved in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), the separator was a glass micro-fiber disk (Whatman GF/F) and the shell was a stainless steel CR2032 coin cell (Pred Materials). We used a constant current constant voltage (CCCV) testing scheme to cycle the cells. The cells were discharged (lithiated) and charged (delithiated) with various cycling currents between 0.05 and 1 V, and between 0.005 and 1 V (vs. Li/Li$^+$). The conducted rate study was carried out with charging rates ranging from C/20–5C. The discharge rates were started at C/20, increased to C/10 and maintained at this rate for subsequent cycling. Charging and discharging were conducted with constant current (CC) cycling parameters.

Material Characterization: An FIB (FEI, NOVA200 dual beam system) equipped with air-lock chamber is used for TEM sample preparation.[16] TEM and EELS analysis was performed with a FEI Tecnai F20 operated at 200 keV. A detailed description of the TEM and EELS characterization procedures can be found elsewhere.[16]


