Freestanding silicon microparticle and self-healing polymer composite design for effective lithiation stress relaxation†

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Self-healing features that mimic the biological mechanisms for self-repair have recently been applied to high-capacity but extreme volume expansion electrode materials such as silicon anodes to overcome the short cycle-life caused by electrical contact loss and active material pulverization. In this study, we adopt a freestanding composite design for effective relaxation of lithiation induced stresses and enhancement of electrochemical reliability. Silicon microparticles are homogenously dispersed and embedded within a self-healing polymer matrix that enables free volume expansion and contraction during lithiation and delithiation. The freestanding electrode, which does not require a separate current collector, demonstrated 91.8% capacity retention after 100 cycles at C/10 rate with an average specific capacity of 2100 mA h g⁻¹ and a gravimetric capacity of 400% that occurs when a large amount of lithium is inserted. This extreme volume expansion causes cracking and pulverization of the electrode materials, which leads to delamination from the electrode and thus a loss of electrical contact as well as unstable solid-electrolyte interphase (SEI) growth; all these factors contribute to premature battery failure.14–19

Many of the next-generation candidate electrode materials demonstrate high theoretical capacities and Si is a prime candidate with a high theoretical capacity of ~4200 mA h g⁻¹ and a relatively low discharge potential (~0.5 V compared to Li/Li⁺), while also having the benefit of the abundance of elemental Si and demonstrating inert properties under atmospheric conditions.8,10,14,18–22 However, Si is especially prone to electrochemical performance loss as a result of extreme volume expansion of ~400% that occurs when a large amount of lithium is inserted. This extreme volume expansion causes cracking and pulverization of the electrode materials, which leads to delamination from the electrode and thus a loss of electrical contact as well as unstable solid-electrolyte interphase (SEI) growth; all these factors contribute to premature battery failure.23,24

For anode materials with extreme volume expansion, nano-structure has been shown to improve the structural durability since the volumetric strain can be easily relaxed in nano-sized structures by more freely expanding in the available free space between the nanostructures.25–29 Chan et al. highlighted the importance of providing free space to allow for volume expansion through nanostructuring and demonstrated an improved cyclability in silicon nanowires in comparison to that of thin films.25 As such, various nanostructures, including...

1. Introduction

Self-healing properties akin to those exhibited in biological systems that are capable of recovering mechanical and electrical properties have demonstrated potential for use in applications such as functional surfaces and wearable electronics to enhance the device lifetime and durability.1–4 Recently, self-healing synthetic polymers have been applied to lithium-ion batteries to prevent performance loss due to fractures as a result of lithiation induced stresses during prolonged cycling.10–13 Lithiation and delithiation of any electrode material is accompanied by volume changes associated with intercalation or alloying, which become more extreme with higher lithium storage. Repeated and/or extreme volume changes may lead to mechanical degradation and, in extreme cases, pulverization, which is a key contributing factor to battery failure.14–19

† Electronic supplementary information (ESI) available: Detailed synthesis and fabrication of the Si-SHP composite; photographic image of the prepared samples; additional electrochemical experiments; and self-healing properties of the composite. See DOI: 10.1039/c7ta11269f
nanowires, core–shell structures and nanoporous structures have been reported to demonstrate high capacity and good cycling stability. However, nanostructures are difficult and expensive to produce in large quantities, making Si nanostructures less desirable for industrial applications. Therefore, it is imperative to develop methods that enable the use of Si microparticles (SiMPs) that are low cost, scalable, and thus more commercially available than Si nanostructures while also demonstrating a high volumetric energy density. The drawback of pure SiMPs, however, is the extremely poor cycling stability that results in over 80% capacity loss over the first few cycles.

The limited cycling lifetime of a Si anode is the result of large volume expansion without sufficient stress relaxation especially when the particles are compacted in the form of a film; high lithiation induced stresses can then cause delamination of the active materials. Another method for resolving this issue is to adopt a polymeric binder with higher elasticity. Various polymer binder candidates for replacing conventional polyvinylidene difluoride (PVDF) have been investigated. Polymeric binders such as polyacrylic acid (PAA), carboxymethyl-cellulose (CMC), and conductive polymers significantly enhanced the capacity and cycling stability due to the elastic nature of the polymeric material. Additionally, the affinity of the polymer functional groups with the native surface oxide on the Si particles allowed for further improvement of cycling stability. However, these polymeric binders eventually underwent irreversible mechanical degradation and delamination due to the repeated extreme volume expansion and contraction of the Si anode and polymeric binders.

Self-healing polymeric binders have recently been introduced to mitigate pulverization and delamination of SiMPs from the current collector by self-healing any fractures in the polymeric binder caused by lithiation induced volume expansion and contraction of SiMPs. Investigations using self-healing polymers (SHPs) as a coating layer that enables spontaneous repair of mechanical degradation to enhance the current collector-Si electrical contact have been reported, where a thin layer of hydrogen bond based SHP was coated on top of SiMPs, 45 wt% SHP and 10 wt% carbon additive. The presence of native oxide on the SiMPs provides better adhesion compared to the conventional PVDF binder enhances the electrochemical performance and stability. However, as SiMPs undergo extreme volume expansion, the integrity of the electrodes and electrical connections during cycling while also enhancing the electrochemical performance and stability.

2. Results and discussion

2.1 Fabrication and characterization of the freestanding SiSHP composite

SHPs are categorized into two types based on their bonding: (1) polymers based on inter-molecular covalent bonding and (2) those based on dynamic inter-molecular bonding such as hydrogen bonding as reported by Leibler et al. Synthesis of SHPs based on covalent bonds requires external sources of energy such as altering the pH of the environment or exposure to elevated temperatures or specific wavelengths of light that increase the internal thermal energy to activate the self-healing of the broken bonds. In addition, microcapsules have been used to self-heal macroscopic mechanical damage, which releases self-repair monomers when the microcapsules are ruptured. However, these methods are irreversible and/or are not suitable for a temperature sensitive lithium-ion battery system. By contrast, polymers based on dynamic inter-molecular bonds are based on weak bonding that can easily be ‘self-healed’ at room temperature and thus are more desirable for temperature sensitive battery applications as they demonstrate repeatable healing capability without application of additional energy. The hydrogen-bond based SHP reported by Leibler et al. that demonstrates abundant hydrogen bonds, viscoelasticity, and stretchability was selected for our composite anode design due to its capability to undergo reversible self-healing even at room temperature. In addition, the SHP composite can self-heal after being completely severed and reattached to recover most of the previous mechanical and electrical properties.

A schematic of the freestanding SiSHP composite electrode consisting of SiMPs and carbon additives in the form of multi-walled carbon nanotubes (MWCNTs) uniformly dispersed within the SHP matrix is shown in Fig. 1. The freestanding SiSHP electrode uses a self-healing mechanism via hydrogen-bonding as shown in Fig. 1b, which enables repair of any fractures within the binder that occur during repeated extreme volume expansion at room temperature. The homogenous dispersion of MWCNTs forms electrically conductive pathways and provides the structural support required to fabricate a freestanding design. In a conventional SiSHP electrode design, all electrodes were fixed to have 45 wt% SiMPs, 45 wt% SHP and 10 wt% carbon additive. The presence of native oxide on the SiMPs provides better affinity with SHP by providing hydrogen bonding sites. The enhanced affinity and elasticity compared to the conventional PVDF binder enhances the contact between Si and the SHP, thereby improving the electrical contact recovery in the event of pulverization and delamination of the SiMPs from the electrode.

The stretchable and spontaneous self-healing ability of the coated SHP improves the mechanical stability and maintains the integrity of the electrodes and electrical connections during cycling. However, as SiMPs undergo extreme volume expansion,
the Cu foil and the neighboring SiMPs effectively act as a constraint in the expansion that therefore develops significant lithiation induced stresses in the SiMPs and the SHP matrix. This is analogous to a thermally expanding metal film that would otherwise be free of stresses on its own but would develop large stresses due to being bonded to the substrate since the film has to match the dimensions of the substrate. Similarly, the coating onto Cu foil necessarily causes constraint on the volume expansion that results in volumetric stresses while our freestanding design will not develop volume expansion induced stresses. Thus, in a conventional design, the SiMPs will eventually be delaminated from the Cu foil, which directly translates to capacity loss. In addition, our freestanding SiSHP composite consists of a homogenous distribution of SiMPs and MWCNTs throughout the SHP matrix that provides sufficient inter-particle spacing as a buffer space for volume expansion.

The morphological characterization of the freestanding SiSHP composite electrode is shown in Fig. 2. SiMPs with diameter ranging from 1 to 5 μm were embedded within the SHP matrix with MWCNTs to create a slurry, which was molded using a Teflon mold for easy release with a depth of 200 μm to fabricate the final freestanding SiSHP composite electrode as shown in Fig. 2a with a more detailed explanation given in Fig. S1.† Surface and cross-sectional SEM images were observed to confirm that SiMPs are uniformly dispersed within the SHP matrix with sufficient separation distance between the SiMPs. Therefore, the freestanding SiSHP composite electrode has the desired microstructure shown in Fig. 1d, Scheme 2. The presence of voids before and after electrochemical cycling is caused by the absence of calendering during fabrication of the SiSHP composite, which leaves macroscopic voids. The SHP matrix provides an elastic and self-healing medium that accommodates the volume expansion of SiMPs while maintaining the electrical contact by preventing delamination of pulverized SiMPs throughout electrochemical cycling as the fractures caused by lithiation induced stresses are repeatedly self-healed.

2.2 Electrochemical characterization of the constrained and freestanding designs

To demonstrate the feasibility and stabilizing effect of the freestanding SiSHP composite electrode design, the electrochemical performance of the freestanding SiSHP electrode was evaluated and compared with that of ‘constrained’ designs consisting of the SHP coated SiMPs on Cu foil (hereafter referred to as the coated SiSHP design) as shown in Fig. 3a and a SiSHP composite cast onto Cu foil (Fig. S1†). Coin cells with lithium metal counter electrodes were employed and galvanostatically cycled between 0.05 V and 1 V. Steel spacers could act as a de facto current collector and were therefore excluded.
The first discharge (delithiation) capacity of the freestanding SiSHP composite reached 2212 mA h g\(^{-1}\), which is lower than the first discharge capacity of the coated SiSHP of 2650 mA h g\(^{-1}\). The difference and the initial increase in specific capacitance in the freestanding design are suspected to be caused by an incomplete activation of SiMPs due to the use of MWCNTs and the thickness of the overall electrode. However, the freestanding design demonstrated excellent cycling stability compared to the coated design, retaining 91.8% of its initial capacity (2030 mA h g\(^{-1}\)) compared to 73.1% retention (1937 mA h g\(^{-1}\)) of the coated SiSHP design after 100 cycles at C/10 rate. If the cycling lifetime is arbitrarily defined as the number of cycles required for the capacity retention to become 80% of the initial value, the freestanding SiSHP composite electrode has a longer cycling lifetime of over 100 cycles in comparison to the coated SiSHP electrode that has a lifetime of 70 cycles. In addition, the freestanding electrode has more than 20 times longer cycle life in comparison to the SiMP electrode embedded in a PVDF binder with the same active material to binder weight ratio (5 cycles, Fig. S2†).

To determine the contribution to the enhancement in cyclability from the freestanding electrode design that allowed for free expansion and contraction, the SiSHP composite was also cast onto Cu foil and put through electrochemical cycling for comparison (Fig. S3†). When the composite is deposited on Cu foil, the composite is constrained by the Cu substrate and is therefore expected to develop stresses in the electrode. The composite electrode cast on the Cu foil substrate exhibited a retention of 78.1% and a cycle life of 85 cycles, which is longer than that of the coated SiSHP electrode but shorter than that of the freestanding electrode. Therefore the drastic increase in capacity retention can be attributed to the change in electrode design that allows for free volume expansion of the SiMPs in the absence of the substrate constraint. SEM images of the constrained electrode after ten electrochemical cycles showed crack formation extending throughout the entire electrode thickness and SiMPs were directly exposed to the electrolyte as the SHP no longer provided uniform coverage. In addition, cross-sectional SEM images revealed delamination of the SiMPs from the Cu foil. By contrast, the freestanding electrode maintained uniform coverage of SiMPs and showed no crack formation throughout the electrode indicating that the freestanding design better managed lithiation induced stresses (Fig. S4†). SiMP loading varied from 0.8 to 1.2 mg cm\(^{-2}\) and exhibited an areal capacity of about 1.9–2.6 mA h cm\(^{-2}\), which is still short of the commercial requirement of lithium-ion batteries (~3 mA h cm\(^{-2}\)), but represents an improvement compared to many of the previous reports.\(^{11,13,26,31,32,35,36,38,39}\) SiMP loading was limited to 1.2 mg cm\(^{-2}\) because a higher SiMP wt% compromised easy handling of the freestanding electrode.

In addition, to confirm the effect of inter-particle distance on the cycling lifetime of the SiSHP composite, a simple investigation was conducted by altering the wt% of the SiMPs and the results are shown in Fig. S5†. The results indicate that the SiMP composition, and by extension the inter-particle distance, have a significant impact on the electrochemical cycling lifetime of the SiSHP composite electrodes. There was a clear relationship between capacity retention and SiMP composition with a smaller wt% demonstrating greater capacity retention. At 20 wt% SiMP composition, the SiSHP composite demonstrated a capacity retention of 97.5% between the 10\(^{th}\) and 20\(^{th}\) cycles while at 60 wt%, the capacity retention decreased to 80.3%.

The rate capability tests shown in Fig. 3c were performed from C/20 to C/2 rate and demonstrated that the freestanding electrode was able to maintain a capacity of around ~1500 mA h g\(^{-1}\) even at C/2 rate and recovered 91.6% of its
initial capacity after rate capability testing, an enhanced recovery compared to the 86.8% of the SiSHP on Cu foil electrode (Fig. S3†). Coulombic efficiency (CE) provides a good indication of stable solid-electrolyte interphase (SEI) formation and the presence of side reactions. The CE of the freestanding SiSHP composite electrode was more than 85%, which improved to about 94% after 100 cycles at C/10 rate. The low CE can be attributed to unstable SEI formation and side reactions from the residual organic solvents within the freestanding composite. In addition, no observable impedance increase occurred after 100 cycles, indicating a stable SEI formation as shown in Fig. 3d.

The most noteworthy benefit of the freestanding design is that a metal foil current collector is removed, which contributes to the higher gravimetric capacity of the overall electrode. Although the specific active material capacities of the two designs are comparable, the difference in gravimetric capacities is drastic. Fig. 3e is a comparison of the gravimetric capacities of the coated SiSHP electrode and the freestanding SiSHP composite electrode including the mass of the respective current collectors, polymer binder, and carbon additives. After the first cycle, the coated and freestanding SiSHP electrodes exhibited gravimetric capacities of 705 mA h g⁻¹ and 1050 mA h g⁻¹ respectively, with the freestanding design.
showing 48% higher gravimetric capacity than the coated design. This trend continued even after 100 cycles, with respective gravimetric capacities of 517 mA h g⁻¹ and 977 mA h g⁻¹ for the coated and freestanding designs, which now indicates 89% enhancement for the freestanding design. Therefore, the freestanding design demonstrates improved gravimetric capacity and cycle life.

2.3 Self-healing of electrochemical and mechanical properties

The elastic properties of the freestanding SiSHP composite electrode were tested by measuring the change in resistance in response to stretching, as plotted in Fig. 4a. The freestanding SiSHP composite electrode was repeatedly strained in tension to 100% and released while measuring changes in resistance. The results indicate that the change in resistance of the composite was negligible even after repeated loading and unloading, indicating that the electrical contact can be reversibly maintained, even compared to the conventional MWCNT–PDMS composite with the same amount of MWCNTs added (10 wt%), shown in ESI Fig. S6,† which underwent an irreversible, drastic increase in resistance. To provide a better perspective on the superior elasticity of the SiSHP, tensile testing comparison of PVDF and SHP samples was conducted, which revealed that PVDF samples could be stretched to up to 15% while the SHP sample could be stretched up to 300%. In addition, repeated in situ resistivity measurements during the tensile test to 100% strain were conducted for 20 stretching cycles that highlighted that the freestanding SiSHP demonstrates excellent viscoelastic properties and stable electrical contact even after repeated loading/unloading analogous to repeated volume expansion during Si lithiation.

The SHP matrix chosen for the freestanding SiSHP composite electrode also demonstrates excellent self-healing properties even at room temperature, as expected. Scratches made to the SiSHP composite were self-healed at room temperature over 60 minutes, demonstrating a reversible self-healing at room temperature as shown in Fig. S7.† Furthermore, the freestanding SiSHP electrode was used to complete a circuit to demonstrate the self-healing capability even after severing and reattaching the composite at room temperature, as shown in Fig. 4b. The self-healing capability of the freestanding SiSHP electrode was further tested by (1) activation for ten charge–discharge cycles at C/10 rate, (2) disassembling the coin

Fig. 4  (a) Normalized change in resistance at different strains. (b) Self-healing demonstration of the freestanding SISHP composite with the composite SISHP used to connect the LED to the battery. (c) Freestanding SISHP composite repeatedly cut and self-healed, to continue with electrochemical cycling. (d) Charge–discharge profiles after each cut and re-assembly of the freestanding SISHP composite anode.
cell in the delithiated state, (3) completely cutting the composite electrode in half, (4) reattaching the electrode with application of palm pressure, and (5) assembling the cell for further cycling. This process was repeated four times for every five cycles under the same conditions and the resulting capacity and voltage profiles after each cut are shown in Fig. 4c and d. Even after repeatedly cutting and reassembling the electrode, the freestanding SiSHP composite electrode demonstrated an excellent capacity recovery indicating that the electrical contact between the two halves was self-healed to its original electrode configuration. After cutting and reassembling the freestanding SiSHP composite electrode at the 10th, 15th, 20th, and 25th cycles, the freestanding electrode retained 95%, 92%, 91%, and 87% of the reference capacity, respectively, thereby demonstrating the electrochemical self-healing capability of the developed freestanding SiSHP composite.

3. Conclusion

To summarize, a freestanding SiSHP composite electrode with a homogeneous dispersion of SiMPs and MWCNTs in a SHP matrix was fabricated and showed a drastic improvement in the gravimetric capacity and cycling lifetime owing to the freestanding composite design and excellent self-healing properties of the polymer matrix. The freestanding design was compared with a conventional design of SiMPs calendared on Cu foil followed by SHP coating. The absence of a substrate enabled free volume expansion with minimal stress development in the freestanding SiSHP composite during electrochemical cycling that resulted in 91.8% capacity retention after 100 cycles compared to 73.1% capacity retention for the coated SiSHP electrode. To further confirm the constraining effect of the Cu foil, the same freestanding SiSHP composite was cast onto Cu foil and tested, and it showed a lower capacity retention of 78.1% after 100 cycles; thus the removal of the substrate constraint in our freestanding design enhanced the cycling stability. The notable outcome of the developed freestanding design is a high gravimetric capacity of 1050 mA h g⁻¹ compared to 705 mA h g⁻¹ for the coated SiSHP design, which is a 48% improvement after the first cycle. The difference was further highlighted after 100 cycles, where the freestanding design exhibited a gravimetric capacity of 977 mA h g⁻¹, which is an 89% improvement compared to 517 mA h g⁻¹ for the coated design. In addition, the freestanding design demonstrated excellent electrochemical performance recovery even after repeatedly cutting and self-healing the composite electrode, which retained 87% of its initial capacity even after four complete cutting-and-self-healing cycles. The newly proposed electrode design of the SiSHP composite therefore allows for not only long cycling lifetime, but also high specific and gravimetric capacities, as well as excellent, repeatable self-healing properties.

4. Experimental section

4.1 Materials

EMPOL 1016 was donated by BASF (80 wt% diacid, 16 wt% triacid). Diethylenetriamine (DETA 99%) and urea (98%) were purchased from Sigma-Aldrich. Silicon microparticles (average particle size 1–5 μm, 99.9%) were purchased from Alfa Aesar. MWCNTs (multiwalled carbon nanotubes) were obtained from CNANO, Inc.

4.2 Synthesis of the self-healing polymer

The hydrogen bond based SHP was synthesized through a condensation reaction as modified by Bao et al. 41.5 g of Empol 1016 and 17 g of DETA were combined at 160 °C for 24 h under an argon atmosphere. The resulting mixture was then dissolved in 150 mL of chloroform and then washed with 150 mL of deionized water and 75 mL of methanol. The chloroform was vacuum removed and then reacted with 300 mg of urea at 135 °C for 40 min.

4.3 Fabrication of the coated SiSHP electrode

The coated SiSHP electrode consists of a Cu foil current collector substrate, a SiMP layer, and a coating of SHP. The SHP was dissolved in chloroform and then mixed with 10 wt% carbon black using a Dual Asymmetric Centrifugal Mixer (2000 rpm, 120 s, THINKY). SiMPs were dispersed in ethanol to form a 1 wt% suspension solution, which was then drop cast onto the Cu foil and then dried at room temperature. The dried SiMP electrode was calendared to form the SiMP electrode with 0.4–0.7 mg cm⁻². For SHP deposition, the SiMP electrode was heated to 60 °C on a hot plate and the SHP–CB mixture was drop cast onto the SiMP electrode to form a uniform coating. The coated SiSHP electrode was then degassed for chloroform removal. The final SiMP to SHP weight ratio was 1 : 1.

4.4 Fabrication of the freestanding SiSHP composite

The freestanding SiSHP composite was fabricated by replacing carbon black with MWCNTs to provide additional structural support in a freestanding design. Much like the coated SiSHP electrode, the SHP was dissolved in chloroform to form a viscous gel-like solution. SiMPs, SHP, and MWCNTs were mixed together at a 45 : 45 : 10 wt% ratio using a Dual Asymmetric Centrifugal Mixer (2000 rpm, 240 s, THINKY). The mixture was then degassed to remove excess chloroform and cast onto a Teflon mold to form the freestanding SiSHP composite with a thickness of several hundreds of micrometers. The composite was cut into the desired electrode size for electrochemical characterization. The same slurry was cast onto Cu foil to fabricate the SiSHP composite electrode on Cu foil.

The silicon–PVDF electrode consisted of the same 45 : 45 : 10 wt% ratio of SiMPs, PVDF, and MWCNTs for direct comparison between electrode designs.

4.5 Material characterization

Surface and cross-sectional morphologies of the electrode designs were confirmed by scanning electron microscopy (SEM) and focused ion beam imaging (FIB, Helios Nanolab 450). A study of changes in resistance during tensile testing was conducted at room temperature and at a strain rate of 1 mm min⁻¹ using a lab-assembled device with a grip-to-grip distance of 50 mm.
4.6 Electrochemical characterization

The electrochemical properties were examined by galvanostatic cycling using 2032 stainless steel coin cells. The respective SiSHP electrode functioned as the working electrode, lithium metal foil (1 mm thick) as the counter electrode, 1 M LiPF$_6$ in ethylene carbonate (EC) and fluoroethylene carbonate (FEC) (1 : 1, v/v) as the electrolyte, and a monolayer polypropylene separator (Celgard® 2400) as the separator. The cells were cycled in constant current (CC) mode at a C/10 rate from 0.05 V to 1.0 V (where 1 C = 3600 mA h g$^{-1}$). Impedance was used to measure the alternating current (AC) at frequencies between 100 mHz and 100 kHz.

4.7 Self-healing characterization

The self-healing properties of the freestanding SiSHP composite were demonstrated first by assembling a coin cell using the freestanding SiSHP composite. The cell was put through ten charge–discharge cycles for stabilization and activation. The cell was then disassembled in an argon glovebox in the delithiated state, cut in half, then reattached with a hand pressure of ~50 kPa, then reassembled, and subjected to five additional charge–discharge cycles. This process was repeated four times to demonstrate the stable electrochemical cycling behavior even after repeated electrode cutting and self-healing.

Conflicts of interest

There are no conflicts to declare.

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