Freestanding Silicon Microparticle and Self-Healing Polymer Composite Design for Effective Lithiation Stress Relaxation

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Supplementary Information



Fig. S1. (a) Molecular structures of the constituent monoacid, diacid, and triacid in the EMPOL 1016 fatty acid product and the use diethylenetriamine and urea. (b) Self-healing mechanism where the hydrogen bonding sites provide fluid inter-molecular bonding that can self-heal in room temperature. (c) Synthesis of self-healing polymer based on condensation reaction as reported by Leibler et al. and Bao et al. (d) Optimization of MWCNT content for freestanding SiSHP composite electrode fabrication and (e) molding freestanding SiSHP composite electrode using Teflon mold.



Fig. S2. Electrochemical properties of the SiSHP composite cast onto Cu foil. (a) Capacity retention and coulombic efficiency off the freestanding SiSHP composite electrode (red) and SiSHP composite on Cu foil (blue) over 100 cycles at C/10 rate. (b) Voltage profile of the 1st and 100th cycle of the SiSHP composite on Cu foil and (c) rate capability at different C-rates.

To confirm the substrate constrain effect on preventing relaxation of lithiation induced stresses, the same SiSHP composite was cast onto a Cu foil for electrochemical cycling with an electrode thickness of ~100 μ m and a schematic is shown inset of Fig. S3a. There was 5% enhancement in capacity retention between the SiSHP composite and reference electrodes, both with Cu foil substrates indicating that the substrate constrain is an important factor to consider in high volume expansion active materials such as Si.



Fig. S3. Comparison of SiMP with PVDF binder with the freestanding SiSHP composite electrode with the same 45 : 45 : 10 wt.% ratio of active material, polymer binder, and carbon additive. Both Si-PVDF and SiSHP electrodes were cycled at C/10 rate. Si-PVDF electrode lost 80 % of its capacity after just five charge-discharge cycles.



Fig. S4. All images are taken from electrodes after 10 electrochemical cycles. Cross-section images of a) constrained coated electrode showing extensive crack formation extending throughout the entire electrode thickness that exposes SiMPs to be in direct exposure to the electrolyte, and b) unconstrained composite electrode showing intact SHP/SiMP composite with no crack formations. Cracks and delaminated SiMPs from Cu foil for constrained coated electrode are shown in c) and d) respectively. The empty spaces of the unconstrained composite electrode are from the lack of calendaring during electrode fabrication. e) and f) show the SiSHP composite after 10 and 100 electrochemical cycles respectively.



Fig. S5. Investigation on the effect of inter-particle spacing was conducted by altering the wt.% of the SiMPs, conduct cross section SEM imaging using FIB, and put through several charge-discharge cycles. A primarily SiMP electrode and electrodes with 20 wt.%, 45 wt.%, and 60 wt.% SiMP content. SEM images reveal that higher SiMP wt.% leads to closer inter-particle distance. Each electrode was cycled under the same conditions mentioned in the Experimental section. Capacity retention was compared between the 10th cycle and the 20th cycles because the first ten cycles were



Fig. S6. a) Change in resistivity with respect to strain for CNT/PDMS (black) and SiSHP Composite (Blue) and only the SiSHP Composite results shown in inset. CNT/PDMS and SiSHP composites of 5 mm x 50 mm x 1 mm (w x I x t) were stretched to 100% strain and measured for changes in resistance. SiSHP Composite had the same wt. % of 45:45:10 of SiMP, SHP, and MWCNT while the MWCNT/PDMS has a composition of 10:90 wt. % of MWCNT and PDMS. Results indicate drastic increase in resistance for the MWCNT/PDMS composite while the SiSHP composite undergoes.

CNT/PDMS composite was fabricated by mixing MWCNT with PDMS using a THINKY mixer system at 2000 rpm for a total of 4 mins. The composite was poured in a stainless steel mold and left to cure in a 50°C oven overnight. **b**) Tensile test results of PVDF and SHP demonstrating that SHP shows much improved elasticity compared to conventional PVDF polymer. **c**) and **d**) Repeated tensile test cycles to 100% strain and return to 0% demonstrating that the SiSHP composite maintains much of the initial conductivity even after repeated stretch cycles.



Fig. S7. Scratches were made on the SHP and SiSHP composite and observed under an optical microscope. Both samples were left at room temperature and the scratches self-healed after 60 minutes. Optical images of (a) self-healing polymer and (b) SiSHP composite electrode before and after healing for 60 minutes at room temperature.