Silicon oxycarbide glass-graphene composite paper electrode for long-cycle lithium-ion batteries

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Silicon and graphene are promising anode materials for lithium-ion batteries because of their high theoretical capacity; however, low volumetric energy density, poor efficiency and instability in high loading electrodes limit their practical application. Here we report a large area (approximately 15 cm × 2.5 cm) self-standing anode material consisting of molecular precursor-derived silicon oxycarbide glass particles embedded in a chemically-modified reduced graphene oxide matrix. The porous reduced graphene oxide matrix serves as an effective electron conductor and current collector with a stable mechanical structure, and the amorphous silicon oxycarbide particles cycle lithium-ions with high Coulombic efficiency. The paper electrode (mass loading of 2 mg cm⁻²) delivers a charge capacity of ~588 mAh g⁻¹electrode (~393 mAh cm⁻³electrode) at 1,020th cycle and shows no evidence of mechanical failure. Elimination of inactive ingredients such as metal current collector and polymeric binder reduces the total electrode weight and may provide the means to produce efficient lightweight batteries.

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Concentrated efforts are currently employed to discover a practical replacement for traditional Li-ion battery electrodes that is, graphite anode and LiCoO₂ cathode with materials that continuously deliver high power and energy densities at high cycling efficiencies without damage1–12. Allying reaction electrodes such as silicon that can deliver as much as 5–10 times higher discharge capacity than traditional graphite, are at the forefront of this research. High capacity electrodes, however, are prone to enormous volume changes (~300%) that generally lead to structural collapse and capacity fading during successive lithiation/delithiation6–12. Recent work has shown that decreasing particle size or electrode nanostructuring allows the electrode to withstand high volumetric strains associated with repeated Li alloying and de-alloying. Pomegranate-inspired carbon-coated Si nanoparticles, yoke shell-structured SiC nanocomposites and Si/C core/shell composites (prepared at low mass loading) have proven to survive several hundred cycles without damage9–13. Yet, electrode composites (prepared at low mass loading) have proven to survive after high current densities (95–98%) and poor capacity retention at high current densities along with high structural stability. Because of their unique nanodomain amorphous structure, SiOC particles offer required chemical and thermodynamic stability and high Li intercalation capacity for the electrode. As a result the electrode (at least 2 mg cm⁻² weight loading) has first cycle charge capacity of 702 mAh g⁻¹ electrode (total weight of electrode considered) and ~470 mAh g⁻¹ electrode (total volume of electrode considered) at 100 mAg⁻¹ electrode and stable charge capacity of 543 mAh g⁻¹ electrode (~363 mAh cm⁻³ electrode) at charge current density of 2,400 mA g⁻¹ electrode. The capacity is ~200 mAh g⁻¹ electrode when cycled at ~15°C. Further, the composite electrode has exceptionally high strain-to-failure (exceeds 2%) as measured in a uniaxial tensile test and the mode of failure differ significantly from pristine rGO papers.

Results

Material synthesis and electrode fabrication. Polymer-derived SiOC ceramic particles were prepared by controlled thermalization of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclosiloxane (TTCS) polymeric precursor while graphene oxide (GO) was prepared by the modified Hummer’s method51 (for details, see Methods section). The polymer-to-ceramic transformation was complete at 1,000°C38. Detailed characterization of cross-linked polymer and resulting SiOC material is presented in Fig. 1a–g. SEM images of SiOC particles in Fig. 1a confirmed average particle size to be ~4 μm (with s.d. = 1.8 μm). X-ray photoelectron spectroscopy (XPS) showed O 1s, C 1s, Si 2s, Si 2p and O 2s peaks for both cross-linked and pyrolyzed SiOC ceramic (Fig. 1b). Close analysis of the deconvoluted silicon band (for Si 2p photoelectrons) in SiOC revealed the emergence of peaks at 103.5 and 102.2 eV, corresponding to SiO₂ and SiO phases, respectively (Fig. 1c). In addition, peaks at 534.5, 533.1 and 532.4 eV corresponding to C = O, SiO₂ and Si–O phases, respectively, were observed in O 1s band (Fig. 1d), whereas the C 1s band (Fig. 1e) was fitted with three peaks at 286.5, 284.5 and 284.7 eV corresponding to C = O, C – Si phases, respectively. Surface elemental composition from XPS was measured to be C = 62.55 at% (50.35 wt%), O = 25.73 at% (27.57 wt%) and Si = 11.72 at% (22.06 wt%). XPS composition after 80 min of depth profiling (with 5 keV Ar ion) showed lower carbon and oxygen content of 50.78 at% (34.47 wt%) and 18.44 at% (16.66 wt%), respectively with Si at 30.78 at% (48.85 wt%) (see Supplementary Fig. 1). Bulk composition of SiOC particles was also determined from combustion and inert gas fusion techniques (see Supplementary Fig. 2a,b and Methods section for details). The composition was found to be C = 51.24 at% (38.3 wt%), O = 19.79 at% (19.7 wt%), lower volumetric changes43,44. Regrettably, the glass-ceramics that show high lithiation capacity are poor conductors of electronic/ionic current and consequently the electrode preparation involves incorporation of conducting agents and binders in order to hold the particles on a metal current collector, a method known as screen printing43–47. Such foil-based electrodes carry the dead weight of conducting agents, polymeric binders, and the metal foil that do not contribute towards the battery capacity.

As an attractive solution to screen printed electrodes, we present our results related to fabrication of a well-organized, interleaved, freestanding, large-area composite anode consisting of SiOC particles supported by crumpled reduced graphene oxide matrix. The electrode delivers higher volumetric capacity than the recently reported pomegranate Si/carbon nanotube (310 mAh cm⁻³ paper-electrode). Large micrometer size reduced graphene oxide (rGO) sheets serve as host material to SiOC particles, providing the necessary electronic path and consistent cycling performance at high current densities along with high structural stability. Because of their unique nanodomain amorphous structure, SiOC particles offer required chemical and thermodynamic stability and high Li intercalation capacity for the electrode. As a result the electrode (at least 2 mg cm⁻² weight loading) has first cycle charge capacity of 702 mAh g⁻¹ electrode (total weight of electrode considered) and ~470 mAh g⁻¹ electrode (total volume of electrode considered) at 100 mAg⁻¹ electrode and stable charge capacity of 543 mAh g⁻¹ electrode (~363 mAh cm⁻³ electrode) at charge current density of 2,400 mA g⁻¹ electrode. The capacity is ~200 mAh g⁻¹ electrode when cycled at ~15°C. Further, the composite electrode has exceptionally high strain-to-failure (exceeds 2%) as measured in a uniaxial tensile test and the mode of failure differ significantly from pristine rGO papers.
The elemental composition obtained from various techniques is summarized in Supplementary Table 1. Raman spectroscopy of SiOC particles was performed to further confirm the existence of the free or excess carbon domains. As shown in Fig. 1f, five peaks could be fitted into the spectrum: D1 or D-band (~1,330 cm⁻¹), D2 (~1,615 cm⁻¹), D3 (~1,500 cm⁻¹), D4 (~1,220 cm⁻¹) and the G-band (~1,590 cm⁻¹) \[^{32}\]. D1, D2 and D4 originate from disordered graphitic lattice (graphene layer edges, surface layers and polyenes and so on) while D3 is associated with amorphous carbon soot. G-band corresponds to the ideal graphitic lattice. In addition, two bumps centered at ~2,640 (2*G overtone) and ~2,915 cm⁻¹ (D + G combination) were also observed (Supplementary Fig. 3). Similarly, Fourier Transform Infrared Spectroscopy (FTIR) analysis also confirmed transformation of TTCS polymer to ceramic SiOC (Fig. 1g)\[^{41}\]. Based on spectroscopic evidence, the predicted chemical structure of the cross-linked polymer and resultant ceramic is presented in Supplementary Fig. 4, which is in agreement with previous work on polymer-derived SiOC\[^{32}\].

H = 5.09 at% (0.31 wt%) and Si = 23.85 at% (41.68 wt%). The elemental composition obtained from various techniques is summarized in Supplementary Table 1. Raman spectroscopy of SiOC particles was performed to further confirm the existence of the free or excess carbon domains. As shown in Fig. 1f, five peaks could be fitted into the spectrum: D1 or D-band (~1,330 cm⁻¹), D2 (~1,615 cm⁻¹), D3 (~1,500 cm⁻¹), D4 (~1,220 cm⁻¹) and the G-band (~1,590 cm⁻¹) \[^{32}\]. D1, D2 and D4 originate from disordered graphitic lattice (graphene layer edges, surface layers and polyenes and so on) while D3 is associated with amorphous carbon soot. G-band corresponds to the ideal graphitic lattice. In addition, two bumps centered at ~2,640 (2*G overtone) and ~2,915 cm⁻¹ (D + G combination) were also observed (Supplementary Fig. 3). Similarly, Fourier Transform Infrared Spectroscopy (FTIR) analysis also confirmed transformation of TTCS polymer to ceramic SiOC (Fig. 1g)\[^{41}\]. Based on spectroscopic evidence, the predicted chemical structure of the cross-linked polymer and resultant ceramic is presented in Supplementary Fig. 4, which is in agreement with previous work on polymer-derived SiOC\[^{32}\].
The composite papers were prepared following a vacuum filtration technique (see Materials section for details and schematic in Supplementary Fig. 5). Samples were labeled as rGO, 10SiOC, 40SiOC, 60SiOC and 80SiOC for rGO paper and GO with 10, 40, 60 and 80 wt% of SiOC in the paper, respectively. The digital camera image and schematic in Fig. 1h highlights the flexibility and structure of the composite paper, respectively.

Morphology of the composite and thermally reduced (annealed) freestanding papers was studied by electron and focused ion beam (FIB) microscopy. The transmission electron microscope (TEM) image (Fig. 1i) showed large micrometer-sized thin GO sheets along with random shape glass-like SiOC particles (also see Supplementary Fig. 6a–e). Large SiOC particles were seen to be covered with smaller nanometer size particles. The graphene platelets seem to occasionally fold and cover individual SiOC particles and other instances show GO being interlayered by SiOC. EDX elemental mapping performed in scanning-TEM mode (Supplementary Figs. 6a–e) confirmed the uniform distribution of Si, O, C in the particles with higher concentration of C observed near the edges possibly due to graphene platelets. For the selected area electron diffraction pattern in Fig. 1j, the multiple spot pattern is a result of polycrystallinity of restacked GO sheets and the faint ring pattern is attributed to amorphous SiOC material. The SEM images of the freestanding papers showed a sheet-like structure with a relatively smooth top surface for rGO paper53–56, which become increasingly rough and porous with higher loading of SiOC particles in the composite (Supplementary Fig. 7a–d). Cross-sectional SEM of the fractured samples revealed ordered stacks of rGO with SiOC particles interlayered between the sheets (Supplementary Fig. 7c–h). Several micrometer sized particles could be seen for 60SiOC specimen along with clumped nanometer sized particles. Nonetheless, mechanically fractured composite papers were largely uneven and showed signs of damage to the interface. To obtain a smooth and defect-free cross-section, the 60SiOC paper was sectioned by means of a FIB milling (see Methods section and Supplementary Fig. 8a for details regarding specimen preparation). The uniform distribution of SiOC particles and wrapping by large-area graphene platelets could be clearly observed in the electron beam (Supplementary Fig. 8b) and ion-beam images (Supplementary Fig. 8c). Elemental mapping by means of EDX (Fig. 1k and Supplementary Fig. 8d–f) further established the inter-layered morphology of the composite. Depending up on the SiOC content, the average thickness of the papers varied between ~20 and 30 μm.

The reduction of GO (non-conducting) to rGO (conducting) was confirmed by use of X-ray diffraction (XRD). As shown in Fig. 1l, both GO and unannealed composite papers, had peaks at 11.05 and 9.8°, corresponding to interlayer spacing of 8 and 12 Å, respectively. Interlayer spacing was large compared with that of graphite (with major peak (002) at 26.53, corresponding to 3.36 Å) because of oxygen functional groups present in GO and water molecules held between the layers. After thermal annealing at 500 °C for 2 h, the paper showed a broad peak at 2θ = 26°, typical of reduced GO material55,56. The broad peak observed in the spectra suggests inhomogeneous spacing between the layers. XRD spectra of cross-linked TTCS and SiOC particles were both featureless, confirming the amorphous nature of these ceramics (hallmark of these materials). Raman spectrum (I_p/I_g) pre and post thermal reduction showed a slight change in accordance with previous reports (Supplementary Fig. 9)39. Reduction of GO to rGO was verified by the disappearance of oxide peaks in the high resolution XPS analysis of C 1s peak (Supplementary Fig. 10).

Thermogravimetric analysis (TGA) was performed to ascertain the mass loading of SiOC in the composite papers. Figure 1m shows the percentage composition of filtered composite paper prior to their thermal reduction. Significant weight loss was observed in the 50–100 °C and 100–400 °C temperature ranges, which is attributed to evaporation of trapped water molecules in the GO and oxygen functionalities, respectively37–39. The weight loss was highest for GO and lowest for 80SiOC (see Supplementary Table 2). Final weight loss in the 400–800 °C range is due to burning of carbon material. Comparatively, the initial weight loss was not observed in thermally reduced samples (mere 1.2% for rGO at 400 °C, Supplementary Fig. 11) that suggests high degree of water removal and oxygen groups by thermal annealing. Approximately 3% and 6–10% residue was noted for GO and rGO material at ~800 °C. As a result SiOC content (or percentage weight remaining) in the thermally reduced composite was higher than unannealed specimens; SiOC content in 10SiOC, 40SiOC, 60SiOC and 80SiOC increased from ~10–30%, ~50–65%, ~65–78% and ~83–92%, respectively. In the traditional method of electrode preparation, active material (including recently reported graphene embedded PDC material) is mixed with polymeric binder and conductive agent in an ~80:10:10 ratio, followed by slurry coating on metal current collector foil47. However, using the present method we have made a freestanding and lightweight electrode, containing up to ~78% SiOC as active material and ~22% of rGO (acting as binder and conductive agent). Paper electrodes were directly utilized as the working electrodes. Electrochemical performance is presented in the following section.

Electrochemical performance. Figure 2a shows charge capacities and columbic efficiency of rGO, 10SiOC, 40SiOC, 60SiOC electrodes asymmetrically cycled at varying charge current densities. For rGO, the first-cycle charge capacity at 100 mAh g⁻¹-electrode was ~210 mAh g⁻¹-electrode; it dropped to ~200 mAh g⁻¹-electrode in the second cycle, and then the charge capacity stabilized at ~180 mAh g⁻¹-electrode after five cycles. When charge current density increased to 2,400 mAh g⁻¹-electrode, charge capacity was retained at ~175 mAh g⁻¹-electrode. Returning the current density back to 100 mAh g⁻¹-electrode, led to the return of higher capacity of 192 mAh g⁻¹-electrode. High irreversible first-cycle capacity results from electrochemical reaction contributed to solid-electrolyte interphase (SEI) layer formation. For the composite electrode, the first-cycle charge capacity increased in correspondence to the percentage of SiOC in the electrode. For example, 10SiOC showed 376 mAh g⁻¹-electrode, while 40SiOC and 60SiOC showed 546 mAh g⁻¹-electrode and 702 mAh g⁻¹-electrode (volumetric capacity of ~470 mAh cm⁻³ electrode), respectively. The 60SiOC capacity was lower than the capacity calculation based on a ‘rule of mixture’ approach (~793 mAh g⁻¹) with constituent rGO (first cycle reversible capacity ~210 mAh g⁻¹) at ~22 wt% as lower bound and SiOC (highest first cycle reversible capacity ~958 mAh g⁻¹ from ref. 46) at ~78 wt% as upper bound. Similar to rGO electrode, when charge current density increased to 2,400 mAh g⁻¹-electrode, composites 10SiOC, 40SiOC and 60SiOC showed high reversible capacity at 296, 417 and 543 mAh g⁻¹-electrode respectively. Capacity retention at 2,400 mAh g⁻¹-electrode of 83.5% (compared with cycle number 5 at 100 mAh g⁻¹-electrode) and first-cycle efficiency of 68% for 60SiOC is among the highest reported performances for a freestanding graphene-based electrode (see Supplementary Table 3 and Supplementary Table 4 for summary and comparison, respectively)14–19,23,25,32,38. When charge current density was lowered again to 100 mAh g⁻¹-electrode at cycle number 31, charge capacity increased to stable values of 304 mAh g⁻¹-electrode (~80% retained), 471 mAh g⁻¹-electrode (~96% retained) and
In order to test cyclic stability of the electrodes, the same cells were subjected to symmetric cycling at a current density of 1,600 mA g$^{-1}$ electrode. Charge capacity for this test is shown in Fig. 2b. Charge capacity of 60SiOC showed some decline as the cells were subjected to prolonged symmetric cycling at 1,600 mA g$^{-1}$ electrode. The capacity decay over the 970-cycle range was observed to be approximately 0.075 mAh g$^{-1}$ electrode per cycle. This decline was not observed in the rGO specimen, thereby demonstrating the importance of graphene in the composite material. Nonetheless, the average composite paper capacity in this range was approximately three times higher than pristine rGO electrode (~170 versus ~58 mAh g$^{-1}$ electrode).

Most significantly, the cell capacities were ~185 (rGO) and 568 mAh g$^{-1}$ electrode (60SiOC) at 1,010th cycle when the current density was brought back to 100 mA g$^{-1}$ electrode and stabilized to 186 and 588 mAh g$^{-1}$ electrode respectively at 1,020th cycle before the tests were stopped for post-cycling analysis. This represents ~94% capacity retention for 60SiOC when compared with capacity value at the 40th cycle prior to beginning of the long-term cycling test (see Supplementary Table 3). No measurable change in cycling efficiency of 60SiOC (~99.6%) was observed during this period. This shows that, even after 1,020 cycles, the composite electrode was robust and continued to function without appreciable degradation.

Supplementary Fig. 12a shows voltage profiles of rGO for the 1st, 2nd and 1,010th cycle. Differential capacity profiles in Supplementary Fig. 12b were similar to previous reports on rGO electrodes, with a primary reduction peak at ~50 mV, a secondary reduction peak at ~(520–560) mV, an oxidation peak at ~(120–130) mV$^{39}$. The peak at ~50 mV, present in all subsequent cycles, is associated with lithiation of graphitic SEI, which exists only in the first cycle. Supplementary Fig. 12c and d show the voltage profile and differential capacity curves of 1st and 2nd cycle of 10SiOC, respectively. The first cycle contained three reduction peaks at around ~50, ~240 and ~520 mV, attributed to RGO lithiation, irreversible Li$_x$SiOC formation, and SEI formation, respectively$^{39,41,45}$. In contrast, only one subtle extraction peak at ~110 mV is observed, which represents RGO de-lithiation with an extended bulge at ~500 mV that represents Li$_x$SiOC de-lithiation$^{38,45–47}$. As the SiOC content increased to 40% (Supplementary Fig. 12e,f) and 60% (see Fig. 2c,d), domination of SiOC lithiation increased, as proven by increased intensity of the irreversible Li$_x$SiOC formation peak at ~(270–300) mV. Peak intensity of rGO de-lithiation at ~120 mV diminished with respect to Li$_x$SiOC.
de-lithiation bulge at ~500 mV. In addition, the 2nd and the 1,010th cycle charge/discharge and differential capacity curves of the electrodes had similar profiles, showing that no new phases formed even after more than 1,000 cycles. More importantly, the efficiency of 60SiOC remained high throughout the cycling test.

Additional rate capability test involving extreme symmetric cycling were performed on freshly prepared 60SiOC paper electrode with even higher mass loading (approximately 3 mg cm$^{-2}$). The data is presented in Supplementary Fig. 13. Stable capacity of ~700 mAh g$^{-1}$ electrode was observed at 100 mA g$^{-1}$ electrode which decreased to ~100 mA g$^{-1}$ electrode at 2,400 mA g$^{-1}$ electrode and showed complete recovery when the current density was brought back to 100 mA g$^{-1}$ electrode. Such stable performance is rarely reported for precursor-derived ceramic materials even on traditionally prepared electrode on copper foil where the current density and capacity are reported with respect to the active material only$^{46-48}$. Tests were also conducted on 80SiOC specimen to ascertain if the charge capacity of the freestanding paper-based electrodes can be improved even further due to higher SiOC content. These attempts, however, were not successful because electrodes prepared at 80% SiOC loading were brittle and showed erratic behavior after only a few initial cycles. First-cycle charge capacity for 80SiOC was ~762 mAh g$^{-1}$ electrode and showed domination of Li$_2$SiOC lithiation (~330 mV) and delithiation (~500 mV) over rGO peaks, similar to other composite electrodes (Supplementary Fig. 14a,b). The 80SiOC electrode began to demonstrate random spikes in charge capacity and efficiency with increased cycle number at high C-rate possibly due to mechanical disintegration and loss of electrical contact due to insufficient rGO loading (Supplementary Fig. 15a). Crack could be observed in the post-cycling SEM images (see Supplementary Fig. 15b–e).

Four-point electrical conductivity measurements were performed and compared for all specimens (for details, see Supplementary Note 1 and Supplementary Fig. 16). Data is summarized in Supplementary Table 5. Although average four-point resistance for 60SiOC (580 $\Omega$) was higher than rGO paper (40 $\Omega$), it still represents an important achievement because TCTCS derived SiOC (under present pyrolysis conditions and for the given composition) was observed to be poor electrical conductor and the improved conductivity of the composite paper (5 $\times$ 10$^{-2}$ S cm$^{-1}$ versus ~10$^{-12}$ S cm$^{-1}$ for SiOC powder$^{41}$) is key to better C-rate characteristics. This is more evident when we compare the C-rate data for SiOC particle electrode prepared on traditional copper current collectors$^{46}$, where the electrochemical capacity was observed to be near zero for cycling current density of 1,600 mA g$^{-1}$.

In addition to room temperature testing, the best performing specimen (that is, 60SiOC) was subjected to electrochemical cycling at sub-zero temperature at ~−15 °C (for details, see Supplementary Note 2). When initially cycled at room temperature (Fig. 2e), the cell had a stable charge capacity of ~600 mAh g$^{-1}$ electrode that then reduced to a stable charge capacity of ~200 mAh g$^{-1}$ electrode when cycled at low temperature. The cell regained ~86% of its initial capacity when it returned to cycling at room temperature.

In order to verify electrode integrity, the cells were disassembled in their lithiated state and the electrode was recovered for additional characterization. The inset in Fig. 2b and Supplementary Fig. 17 show the digital photograph and SEM image of the cycled electrodes. Post-cycling Raman spectroscopy data is presented in Supplementary Fig. 18 and Supplementary Table 6. No evidence of surface cracks, volume change, or physical imperfections were observed in the SEM images, suggesting high mechanical/structural strength of the composite paper towards continuous Li-cycling which could be attributed to unique structure of the electrode as shown in Fig. 2f. In all cases, evidence of SEI formation due to repeated cycling of Li-ions was observed. Contamination in the specimen, indicated by arrows, was a result of residue of glass separator fibers. The electrodes were briefly exposed to air during the transfer process, resulting in oxidation of Li, which appeared as bright spots in the images due to non-conducting nature.

To illustrate the kinetics of charge/discharge of the composite paper, Galvanostatic intermittent titration cycling was performed for the 60SiOC electrode at room and low temperature (for details, see Supplementary Note 3). Acquired DLi$^+$ varied between ~10$^{-14}$ and ~10$^{-15}$ m$^2$s$^{-1}$ during insertion and extraction (Supplementary Fig. 19). These values are comparable with values reported for polymer-derived SiOC (Kasper et al. 10$^{-13}$ to 10$^{-15}$ m$^2$s$^{-1}$)$^{44}$. In addition, total polarization potential and time dependent change in open-circuit voltage (OCV) at various states of charge were inferred for these experiments, as shown in Supplementary Fig. 20a–d. Reaction resistance to Li insertion and extraction from the 60SiOC electrode was calculated by taking a ratio of OCV to the current density (Supplementary Fig. 20e.f). Reaction resistance was fairly constant at 2 Ohm g$^{-1}$ during room temperature insertion. However, it increased exponentially to 8 Ohm g during Li extraction in the 1.5–2.0 V range, which highlights the difficulty in extracting the very last Li atoms from amorphous SiOC structure (Fig. 2g). Density of state calculations (Supplementary Fig. 21) show that Li is stored at several energy levels in the amorphous SiOC structure, with majority of the insertion occurring in the 0.0–0.5 V range. Further, a voltage hysteresis of ~0.5 V exists during the extraction half, which could be attributed to the hydrogen (H-terminated edges of free carbon phase) that are generally present in the SiOC derived from thermal decomposition of organosilicon polymers. H content in pyrolyzed ceramic particles was measured to be ~0.25–0.3 wt% (for details, see Methods section, Supplementary Fig. 2, Supplementary Table 1). Galvanostatic intermittent titration performed at low temperature (~−15 °C) showed DLi$^+$ values in the ~ (10$^{-15}$ to 10$^{-13}$) m$^2$s$^{-1}$ range during Li-ion insertion and extraction (Supplementary Fig. 22). The total polarization potential, time dependent change in OCV at various states of charge performed at ~−15 °C and corresponding reaction resistance plots are included in Supplementary Fig. 23.

**Mechanical strength of the electrode.** Static uniaxial tensile tests were conducted to quantify the strength and strain-to-failure for the freestanding composite papers by use of a custom-built setup. Figure 3a shows a schematic of the test setup, in which the load cell is attached to a digital meter, connected to a transducer electronic data sheet in order to transfer the data to host computer through an RS232 serial port using a program written in MATLAB. Engineering stress–strain plots and tensile modulus, derived from load–displacement curves for various paper electrodes are compared in Fig. 3b,c, respectively. The rGO sample showed average tensile strength of ~10.7 MPa at a failure strain of 2.8%, while 60SiOC sample had tensile strength of ~2.7 MPa at a strain of 1.1%. Low tensile strength of the 60SiOC specimen was expected considering that it contained only ~20% rGO. Overall, strength and modulus for these crumpled composite papers was lower than GO and rGO papers prepared from techniques other than high temperature reduction $^{33,34}$. However, the strain-to-failure was almost 5 to 10 times higher than a typical GO, rGO or rGO-composite paper, suggesting that crumpled composite papers may be able to sustain larger volume changes. Surface analysis using SEM of rGO (Fig. 3d) showed occurrence of micro features after tensile test, which we suggest, are due to
rearrangement of rGO sheets under tensile load. These micro features are assumed to be due to curling of individual graphene sheets on the top surface when they lose contact with the sheets below them. However, for 60SiOC in Fig. 3e, ceramic particles acted as the point of fracture and caused rGO sheets to separate without stretching, as proven by SEM images that show no distinguishable changes before and after tensile test. Supplementary Fig. 24a–h are the top and cross-sectional view SEM images of fractured surface. The rGO because of higher elasticity had an irregular crumpled appearance, but composite papers were more brittle and had sharper cross-section. Mode of fracture in rGO and 60SiOC papers differed significantly, as presented in Supplementary Movies 1 and 2. A loud distinct sound indicated almost instantaneous fracture of the rGO specimen, accompanied by curling of both ends of the fractured paper. Fracture of 60SiOC specimen was similar to a thin plate with an edge crack, the crack propagation could be clearly observed. In addition, stress lines could be observed only in the rGO specimen, radiating from one clamp to another and indicating distribution of stress throughout the length of the specimen. These observations are explained with the help of a schematic in Fig. 3d,e. Ex situ Raman analysis (Supplementary Fig. 25) from the top surface of the specimens before and after tests showed increase in average intensity ratio of the $I_d$ and $I_g$ peaks for rGO (0.88 versus 1.02) while the ratio was largely unaffected for composite specimen.

**Discussion**

Electrochemical characterization shows that 60SiOC is best long-term cycling electrode with reversible capacities of $\sim 702 \text{ mAh g}^{-1}$ electrode at 1st cycle and $\sim 588 \text{ mAh g}^{-1}$ electrode at 1,020th cycle, respectively. Although 80SiOC offers highest first reversible capacity of $\sim 762 \text{ mAh g}^{-1}$ electrode, it undergoes capacity fading and mechanical damage after few initial cycles at high currents. Hence, the capacity and cycling stability are affected by the relative amounts of SiOC and graphene in the composite, respectively. We ascribe the superior electrochemical performance of 60SiOC electrode to remarkable physical and chemical properties of its constituents and the unique
morphological features of the paper. Because graphene sheets in 60SiOC occupy larger volume in the composite, well-dispersed GO sheets during the layer by layer filtration process arrange themselves around the SiOC particles to form a flexible composite paper. TEM (Supplementary Fig. 6), SEM (Supplementary Fig. 7) and FIB (Supplementary Fig. 8) characterization shows that morphology of the composite paper is planar and porous. The porous design therefore facilitated liquid electrolyte to reach the very interior of the electrode thereby providing easy path for solvated ions to be transported on to the surface of SiOC particles. Further, rGO because of its high electrical conductivity and mechanical flexibility provided an electrically conducting agent reduces the total electrode weight and provides the means to produce high performance batteries. 

Preparation of GO and SiOC composite paper

Preparation of GO and SiOC composite paper consisting of SiOC glass-ceramic particles supported in rGO matrix as a stable and durable battery electrode. The porous 3-D rGO matrix served as an effective current collector and electron conductor with a stable chemical and mechanical structure while, embedded amorphous SiOC particles actively cycled Li-ions with high efficiency. Elimination of inactive ingredients such as metal current collector, non-conducting binder and conducting agent reduces the total electrode weight and provides the means to produce high efficient lightweight batteries.

**Methods**

**Preparation of polymer derived SiOC ceramic.** SiOC was prepared through the polymer pyrolysis route, liquid 1,3,5,7-tetramethyl-1,3,5,7-tetrahydridycloctetrasiloxane (TTCS, Gelest, PA) precursor (with 1 wt% dicumyl peroxide added as the cross-linking agent) was cross-linked at 380 °C in argon for 5 h, which resulted in a white infusible mass. The infusible powder was ball-milled in to fine powder and pyrolyzed at 1,000 °C for 10 h in flowing argon resulting in a fine black SiOC ceramic powder.

**Chemicals.** Sodium nitrate (99.2%), potassium permanganate (99.4%), sulfuric acid (96.4%), hydrogen peroxide (31.3% solution in water), hydrochloric acid (30% solution in water) and methanol (99.9%) were purchased from Fisher Scientific. All materials were used as received without further purification.

**Preparation of GO and SiOC composite paper.** Modified Hummer’s method was used to make GO.1 A total of 20 ml colloidal suspension of GO in 1:1 (v/v) water and isopropanol was made by sonication. Varying weight percentages of SiOC particles (with respect to GO) were added to the solution and the solution was sonicated for 1 h and stirred for 6 h for homogeneity of mixing. The composite suspension was then filtered by vacuum filtration through a 10 μm filter membrane (HPLC grade, Millipore). The GO/SiOC composite paper obtained was carefully removed from the filter paper, dried, and thermally reduced at 500 °C under argon atmosphere for 2 h. The large area paper with 60SiOC composition (large field of view, cut into rectangular strip) was similarly prepared by use of a Büchner funnel with a polypropylene filter paper (Celgard). The heat-treated paper was then punched (cut) into small circles and used as working electrode material for Li-ion battery half-cells.

**Coin cell assembly and electrochemical measurements.** Li-ion battery coin cells were assembled in an argon-filled glove box (1 M LiPF6 (Alfa Aesar) in 1:1 (v/v) dimethyl carbonate:ethylene carbonate (ionic conductivity 10.7 mS cm−1)) as the electrolyte. A 25 μm thick (19 mm diameter) glass separator soaked in electrolyte was placed between the working electrode and pure Li foil (14.3 μm diameter, 75 μm thick) as the counter electrode. Washer, spring, and a top casing were placed to complete the assembly before crimping.

**Instrumentation and characterization.** SEM of SiOC powder was carried out on a Carl Zeiss EVO MA10 system with incident voltage of 5–30 kV. TEM images were digitally acquired by use of a Phillips CM100 operated at 100 kV. Elemental mapping was performed by using a 200 kV S/TEM system (FEI Osiris) equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector. Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAADF) and Super-X windowless EDX detector system equipped with chemiSTEM technology, a high angle annular dark field (HAAADF) and Super-X windowless EDX detector system equipped with...
Hydrogen content in SiO-C ceramic was also confirmed by use of another equipment based on combustion/thermal conductivity detector method, CE-440 Elemental Analyser (Exeter Analytical, UK). Combustion of the weighed sample (1.8056 mg of fine powder) was carried out in the instrument chamber in pure oxygen under static conditions. Helium carried the combustion products through the analytical system to atmosphere. Between the thermal conductivity cells absorptive layer retained water from the sample gas. The differential signal read before and after the trap reflected the water concentration and, therefore, the amount of hydrogen in the original sample. The hydrogen content by this method was observed to be 0.25 wt% with an error of 0.06%. TGA was performed using Shimadzu 50 TGA (limited to 800 °C). Samples weighing ~2.5 mg, were heated in a platinum pan at a rate of 10 °C min⁻¹ in air flowing at 20 ml min⁻¹. Electrical conductivity measurements were carried out by use of a four-point probe setup and Keithley 2636A (Cleveland, OH) dual channel sourcemeter in the Ohmic region. Electrochemical cycling of assembled cells was carried out using multichannel Battery Test Equipment (Arbin-BT2000, Austin, TX) at atmospheric conditions.

Mechanical testing. Static uniaxial in-plane tensile tests were conducted in a custom-built test setup. One end of the setup was connected to a 1N load cell (ULC Instruments) and the other end was clamped to a computer-controlled translation stage (M-111.2D/G from PI). The entire setup was located on a bench with self-adjusting feet. All tensile tests were conducted in controlled strain rate mode with a strain rate of 0.2% min⁻¹. Paper electrodes were cut (punched out) into rectangular strips of ~5 x 15 mm² for testing without any further modification.

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Author contribution

L.D. prepared all composite specimens, performed electrochemical testing, raman spectroscopy, low magnification TEM and mechanical testing. U.B. assisted L.D. with cell assembly. R.B. synthesized SiOC particles. G.S. conceived the idea, designed the experiments, performed elemental analysis/mapping and wrote the manuscript with inputs from L.D. All authors discussed the results and commented or revised the manuscript.

Additional information

Competing financial interests: The authors declare the following competing financial interest(s): G. S., R. B. and L. D. have filed for a provisional patent: U.S. Provisional Patent Application 61/817,626—Flexible Silicon oxycarbide Graphene Composite Electrodes for High Rate Performance Lithium-ion Batteries; Filed 30 April 2013.

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