Bioinspired mechanically interlocking holey graphene@SiO₂ anode

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Abstract
Mechanically interlocking structures that can enhance adhesion at the interface and regulate the stress distribution have been widely observed in biological systems. Inspired by the biological structures in the wings of beetles, we synthesized a holey graphene@SiO₂ anode with strong mechanical interlocking, characterized it electrochemically, and explained its performance by finite element analysis and density functional calculations. The mechanically interlocking structure enhances lithium-ion (Li⁺) storage by transmitting the strain from SiO₂ to the holey graphene and by a mechano-electrochemical coupling effect. The interlocking fit hinders the abscission of SiO₂ and the distinctive structure reduces the stress and strain of SiO₂ during (de)lithiation. The positive mechano-electrochemical coupling effect preserves the amount of electrochemically active phase (LiₓSi) during cycles and facilitates Li⁺ diffusion. Therefore, the capacity shows only a slight attenuation after 8000 cycles (cycling stability), and the specific capacity is ~1200 mA h g⁻¹ at 5 A/g (rate-performance). This study furnishes a novel way to design high-performance Li⁺/Na⁺/K⁺/Al³⁺ anodes with large volume expansion.

KEYWORDS
holey graphene, mechanically interlocking, mechano-electrochemical coupling effect, simulation, SiO₂ anode
1 | INTRODUCTION

Lithium-ion (Li⁺) batteries are widely used in modern society. In recent years, many high-capacity anodes, such as Si, SiO₂, Fe₃O₄, Fe₂O₃, and MnO₂,[1,2] have been developed; however, volume expansion of the anode can cause capacity decay, which is a major obstacle in practical applications.[3,4] During lithiation and delithiation, the volume expansion and stress can pulverize the active materials, exfoliate some of the active materials, decrease conductivity, and impede the diffusion of Li⁺; furthermore, the continuous formation of electrochemically inactive phases can gradually deteriorate the capacity.[5-7] These problems diminish the rate and cycling performance of the high-capacity anodes.[8] Due to its unfavorable particle dimension increase during cycling, SiO₂ is selected as a representative case to study in the present work.

A biological mechanism that can enhance interface adhesion and regulate stress distribution is the physical interaction of mechanically interlocked constituents at interfaces.[9,10] Mechanical interlocking is widespread in the natural world. For example, the mechanical interlocking of roots to the soil allows trees to withstand severe weather conditions,[11] and the mechanical interlocking of beetles’ wings maximizes shear friction and minimizes lift-off during repeated folding and unfolding,[12] the interlocking system also is found in the heads and necks of dragonflies.[13] Inspired by those cases, by the excellent combination of mechanical strength and flexibility of graphene, and by the low cost, availability, and high theoretical specific capacity of SiO₂, we here examine graphene/SiO₂ composites with enhanced interface adhesion promoted by the mechanically interlocking structure as a way to decrease the internal stress of SiO₂ anodes during cycling. Moreover, we propose that the recycling efficiency is increased by a mechnano-electrochemical coupling effect such that Li⁺-uptake as recyclable Li₂Si is favored over Li-uptake as unrecyclable species.[6]

To accomplish the interlocking, we prepared an HG@SiO₂ anode by depositing SiO₂ in holey graphene (HG) (Figure 1A), and for comparison, we also prepared G@SiO₂ containing pristine graphene. Thermogravimetric analysis (TGA) shows ~30 wt% of graphene in both composites (Supporting Information: Figure S1).

Compared with the material synthesized by a common encapsulating strategy (Figure 1B), the mechanically interlocked material relieves the stress on SiO₂ by force transmission from SiO₂ to HG. This prevents or decreases the abscission and pulverization of SiO₂ during cycling. Moreover, the positive mechnano-electrochemical coupling effect induced by mechanical interlocking preserves the amount of electrochemical active phase (Li₂Si) during cycles and facilitates Li⁺ diffusion. Therefore, the HG@SiO₂ anode exhibits excellent cycling stability and rate performance.

2 | RESULTS AND DISCUSSION

We employed finite element analysis to explore the feasibility of the proposed design concept with established models (Supporting Information: Figure S2).[14-16] After lithiation, the SiO₂ in G@SiO₂ expands uniformly (Figure 1D), and the maximum stress and displacement are as high as ~1.4 × 10¹¹ N/m² and ~10.5 μm (Figure 1F), respectively. For the HG@SiO₂, the SiO₂ closest to the interlocking interface has the smallest deformation; the stress in SiO₂ is below 0.5 × 10¹¹ N/m² (Figure 1C) and the maximum displacement is ~4.2 μm (Figure 1E). Moreover, the graphene in G@SiO₂ is almost strain-free and undeformed, while that in HG@SiO₂ is elongated and stress-bearing (~2 × 10¹¹ N/m²). Similar features are seen in the volume strain distribution diagrams (Supporting Information: Figure S3). This analysis shows that the mechanical interlocking structure can effectively reduce the stress and strain of SiO₂ during lithiation. In addition, the stress is ~4.7 × 10¹¹ N/m² at the interface between graphene and SiO₂ (inset in Figure 1C); this indicates a snug fit that can boost the cycling stability by preventing SiO₂ from exfoliating during cycling. The C 1s spectra features in the X-ray photoelectron spectroscopy (XPS), of the two samples (Supporting Information: Figure S4a,b) can be deconvoluted into C–C/C–C (284.6 eV), C–OH (286.6 eV) and C=O (288.6 eV),[17] while the Si–O–C bond has not been found. This indicates that the interfaces between SiO₂ and graphene (G) and between SiO₂ and HG are dominated by noncovalent interactions, which is consistent with the models in finite element analysis.

The reduced stress and displacement are also important for Li⁺ transport. When lithiation causes volume expansion, the lithiated portion of SiO₂ can compress the pristine part, causing compressive strain.[6] Our density functional calculations indicate that the diffusion of Li⁺ in SiO₂ with 0.5% strain has an energy barrier of 3.99 eV (Figure 1G), which is higher than the barrier of 2.32 eV in strain-free SiO₂ reported in our previous work.[12] When the strain is increased to 3% and 5%, the energy barrier also is increased to 4.78 and 5.35 eV, respectively (Supporting Information: Figure S5). These calculations indicate clearly that the reduced stress makes Li⁺ diffusion more facile.

Scanning electron microscope (SEM) images show that the pristine graphene has a smooth surface, and the HG is dimpled (Supporting Information: Figure S6). We showed in previous work that the defect density,
chemical composition, and conductivity show a small difference between HG and G.\textsuperscript{[17]} Transmission electron microscope (TEM) morphology and corresponded elemental mappings of HG@SiO\(_2\) (Figure 2A–D) and G@SiO\(_2\) (Supporting Information: Figure S7) are consistent with the SEM results (Supporting Information: Figure S8). Energy dispersive spectroscopy (EDS) indicates that after SiO\(_2\) is deposited, it encapsulates both G and HG uniformly, and the holes in HG@SiO\(_2\) are filled with SiO\(_2\). X-ray diffraction (XRD) patterns for both materials show a peak at \(\approx 23\) degrees arising from amorphous SiO\(_2\),\textsuperscript{[18]} but the characteristic peaks of graphene (G or HG) are not observed due to its disorderly stacking when the SiO\(_2\) is introduced (Supporting Information: Figure S9).\textsuperscript{[19]}

Confirmation that mechanically interlocking structures are formed is provided by the TEM, and Figure 2A shows uneven contrast in HG@SiO\(_2\) and Figure 2E shows uniform contrast in G@SiO\(_2\). Figure 2G divides the TEM image of the selected portion of HG@SiO\(_2\) in

**FIGURE 1** Design, mechanical analysis, and energy profile. Design schematic of (A) HG@SiO\(_2\) and (B) G@SiO\(_2\). Strain distribution and shape change of (C) HG@SiO\(_2\) and (D) G@SiO\(_2\) after lithiation; the scale factor is a parameter to control the display of the strain-stress plot in COMSOL. Displacement distribution of (E) HG@SiO\(_2\) and (F) G@SiO\(_2\) after lithiation. (G) Energy profile for Li\(^+\) diffusion in SiO\(_2\) with 0.5\% strain; the diffusing Li\(^+\) are circled.
Figure 2F into three parts. The C, Si, and O signals are observed in part II, indicating that SiO₂ encapsulates the graphene. In part III, the C signal disappears (the weak C signal there is from the copper mesh matrix and is similar to the signal in part I) while the Si and O signals remain, indicating that the interlocking microstructure of Figure 1A is achieved. To further confirm the interlocking microstructure, an HG@SiO₂ nanosheet was cut by a focused ion beam, as shown in Supporting Information: Figure S10a. The morphology and EDS elemental mapping of the exposed fresh cross section are shown in Supporting Information: Figure S10b–e, which show that the C, Si, and O elements are distributed in the whole cross-section, indicating that the SiO₂ fills the holes rather than deposits on the surface. This further supports the interpretation that the microstructure is interlocking. The formation of holey graphene is due to the oxidative-etching reactions, which initiate and propagate within the oxygenic defect regions, leading to the preferential removal of oxygenated carbon atoms and generation of carbon vacancies that gradually expand into nanopores in the basal plane of graphene. The edges of holes have high activities, and they are active sites for SiO₂ to nucleate and grow; the SiO₂ can fill the holes to
form the mechanical interlocking structure.\[^{17,20}\] We believe that the possibility of preparing a mechanically interlocking structure is universal provided that one material (the matrix) is porous with holes, and another material (the filling material) can fill the holes. In addition to the method proposed in this study, other possible strategies to deposit the filling material are chemical vapor deposition (CVD), physical vapor deposition (PVD), and electroplating.

Electron paramagnetic resonance (EPR) spectra of G@SiO\(_2\) and HG@SiO\(_2\) (Figure 2H) yield \(g\) values of around 2, indicating some oxygen vacancies. The XPS O 1s and Si 2p spectra also show the formation of oxygen vacancies (Supporting Information: Figure S4). Density functional calculations indicate that the energy barrier for an oxygen atom to escape from the surface of SiO\(_2\) is 4.04 eV (Figure 2I), much smaller than that for a deep site, where the barrier is 12.63 eV (Figure 2I). Therefore, the oxygen atoms on the surface are easier to escape and form oxygen vacancies. G@SiO\(_2\) and HG@SiO\(_2\) are sheet-like nanomaterials with large surface areas, and the deposits of SiO\(_2\) into G and HG were carried out in an alkaline solution, such that it was favorable for the SiO\(_2\) sites on the surface to be etched to form oxygen vacancies. Note that the etching strategy is also used to introduce oxygen vacancies in other oxides, such as TiO\(_2\).\[^{21}\] The tendency for oxygen vacancies to be formed near the surface, when combined with the very small thickness of the samples, makes the existence of vacancies understandable. Some previous work has shown that the introduction of oxygen vacancies in active materials is a promising way to improve the specific capacity, lower the energy barrier of Li\(^+\) diffusion, and increase the conductivity.\[^{22,23}\]

The cycling and rate performance of G@SiO\(_2\) and HG@SiO\(_2\) are shown in Figure 3A,B, and the discharge–charge curves are in Supporting Information: Figure S11. The specific capacities of HG@SiO\(_2\) are higher than those of G@SiO\(_2\) and are about 2300, 2200, 2000, 1500, and 1200 mA h g\(^{-1}\) at current densities of 0.2, 0.5, 1, 3, and 5 A/g, respectively.

The specific capacity retention (SCT) is based on Figure 3B and is calculated by

\[
\text{SCT} = \frac{C_x}{C_{0.2}} \times 100\%,
\]

where, \(C_{0.2}\) and \(C_x\) represent the average specific capacity at current densities of 0.2 and \(x\) A/g, respectively.
HG@SiO$_2$ has higher SCT values than G@SiO$_2$ (Supporting Information: Figure S12). In particular, the SCT values of HG@SiO$_2$ vary from 95% at 0.5 A/g to 49% at 5 A/g.

The cyclic voltammetry (CV) curves of G@SiO$_2$ and HG@SiO$_2$ are very similar (Supporting Information: Figure S13), which indicates that the Li$^+$ storage mechanism is unchanged by the introduction of a mechanical interlocking structure. The cycling stability of the two electrodes is shown in Figure 3A. The specific capacity of G@SiO$_2$ fades to 300 mA h g$^{-1}$ after 1200 cycles, whereas the specific capacity of HG@SiO$_2$ remains much higher, 810 mA h g$^{-1}$ after 8000 cycles. Supporting Information: Tables S1 and S2 compare the cycling and rate performance of HG@SiO$_2$ to that of recently reported silica anodes, and we see that the performance is outstanding.

Electrochemical impedance spectroscopy (EIS) (Figure 3C,D) shows semicircle-like elements at the medium-to-high frequency and an increase in reactance at low frequency. A smaller radius of the semicircle corresponds to smaller charge transfer resistance, and the low-frequency increase is associated with resistance to bulk diffusion.[24] A comparison of Figure 3C,D shows that HG@SiO$_2$ has smaller charge transfer resistance. The semicircles in these plots increase in size with cycle number because of the buildup of solid electrolyte interphase (SEI) during cycling.[25] After 500 cycles, the surface of the G@SiO$_2$ electrode is broken into small pieces, but the surface of the HG@SiO$_2$ electrode is relatively intact (Supporting Information: Figure S14). Moreover, the single HG@SiO$_2$ nanosheet (after 500 cycles) is relatively intact (Figure 4E), while the SiO$_2$ fractures and is stripped from graphene for the G@SiO$_2$ nanosheet (Figure 4F). These results imply that the expansion of SiO$_2$ is restrained[56] and the SiO$_2$ is interlocked with HG.

The low-frequency portion of the EIS indicates that the Li$^+$ diffusion is more facile in HG@SiO$_2$ than in G@SiO$_2$. This is also shown by the higher values of the ratio of the voltage change for a current pulse to the voltage change during a current pulse in galvanostatic intermittent titration technique (GITT) measurements (Supporting Information: Figure S15). The excellent rate-performance of HG@SiO$_2$ can be explained by the low strain in SiO$_2$ since the density functional calculations show that lower strain gives lower diffusion barriers.

The strain on the anode can be assessed by monitoring the G-band of graphene in Raman spectra, which usually shifts to a lower wavenumber under tensile strain.[27] Therefore, ex-situ Raman spectra were measured at various voltages to compare the strain on the two kinds of the anode.[28] This experiment was conducted with the half-cell configuration in which Li metal is the counter electrode (in this case the HG@SiO$_2$ is technically the anode, but it is conventional to still call it the anode and to treat this as a test of anode performance for the case where the supply of Li$^+$ is not limited by the capacity of the counter electrode). In the half-cell experiment, the discharge is the lithiation of HG@SiO$_2$, and the charging process is the delithiation of HG@SiO$_2$. During lithiation, Li$^+$ gradually alloys with HG@SiO$_2$ with voltage changing from 1 to 0.01 V, and during delithiation, Li$^+$ is gradually removed with voltage changing from 0.01 to 1 V (Figure 4B). The degree of lithiation depends only on the voltage. Figure 4C shows that during lithiation, the graphene G-band in HG@SiO$_2$ gradually shifts to a low wavenumber, and it recovers when the voltage is charged back to 1 V (delithiation). However, the graphene G-band in G@SiO$_2$ does not change as the voltage changes (Figure 4D). This implies that the HG in HG@SiO$_2$ is stretched during lithiation and recovers during delithiation, whereas G in G@SiO$_2$ has no geometric change. The result is consistent with the finite element analysis indicating that the strain is transmitted from SiO$_2$ to HG by the mechanical interlocking structure. The strain on graphene is reversible due to its flexibility, and reversibility enhances cycling stability.

Finally, we consider the mechano-electrochemical coupling effect. When the cell is discharged to 0.01 V, reversible Li$_2$Si is formed in SiO$_2$ anodes.[29,30] The reversible Li$_2$Si and inactive lithium compounds (LiF, Li$_2$O, and LiCO$_3$) can be distinguished based on their XPS Li 1s spectra (Supporting Information: Figure S16). Based on the integrated areas under the peaks corresponding to the various species, the percentage of Li that is in the reversible Li$_2$Si form is calculated after the 5th, 100th, and 200th cycles, and the results are given in Figure 4G. For G@SiO$_2$, the reversible Li$_2$Si sharply decreases from 30% to 7.4%, while that for HG@SiO$_2$ remains close to 30% even after 500 cycles. To understand this, we calculated the energies of possible Li$_2$Si crystals (Supporting Information: Figure S17) without and with stress (equivalent to a hydrostatic pressure of 1 GPa), and their energies are shown in Supporting Information: Table S3. The energy differences (the energy of the unstressed material minus the energy of the stressed material) are calculated and shown in Figure 4H, and the energy differences are all negative, indicating that all Li$_2$Si are more stable in the free state. Figure 4H also gives the energy difference between the free-state and stressed state of Li$_2$O, which is the main inactive (nonrecyclable) lithium compound formed at the SiO$_2$ anode.[38] The energy difference for Li$_2$O is much less than that of each Li$_2$Si, indicating that lowering the stress lowers the energy more for the recyclable forms (Li$_2$Si) than for the nonrecyclable form (Li$_2$O). Therefore, the reduced stress in the holey material
would favor the formation of Li$_x$Si. Supporting Information: Table S3 also shows low energy differences for Li$_4$SiO$_4$ and Li$_2$SiO$_3$, which have been identified previously as inactive Li species that could potentially be produced.[8] This mechano-electrochemical coupling effect facilitates the reversibility of electrochemical active phases Li$_x$Si and the transfer of Li$^+$. 

### 3 | CONCLUSIONS

An HG@SiO$_2$ anode with a bioinspired mechanical interlocking structure is predicted and fabricated. The mechanically interlocking structure induces an interlocking fit and reduces the stress and attendant strain on SiO$_2$, thereby preventing the SiO$_2$ from exfoliation and pulverization. Moreover, the positive mechano-electrochemical coupling effect preserves the amount of electrochemically active phase (Li$_x$Si) during cycles and facilitates the Li$^+$ diffusion. The enhanced mechanism is schematically illustrated in Figure 4A. In conclusion, improved stress mechanics ameliorates the negative consequences of large volume expansion, and a favorable mechano-electrochemical coupling effect has a positive effect on recycling stability. Consequently, the specific capacity of HG@SiO$_2$ shows only slight attenuation after 8000 cycles, and the HG@SiO$_2$ presents excellent rate
performance. This study provides a novel way to design and prepare high-performance anodes with large volume expansion.

**AUTHOR CONTRIBUTIONS**

Fei Wang proposed methodology, carried out experiments and simulations, and wrote the paper. Xiaobin Liao provided suggestions for the COMSOL and density functional simulations and reviewed the paper. Haoyu Wang provided the software of COMSOL and reviewed the paper. Yan Zhao, Jian Mao, and Donald G. Truhlar provided supervision, revision of the paper, and resources.

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**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

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**SUPPORTING INFORMATION**

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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