Supremely elastic gel polymer electrolyte enables a reliable electrode structure for silicon-based anodes

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Silicon-based materials are promising anodes for next-generation lithium-ion batteries, owing to their high specific capacities. However, the huge volume expansion and shrinkage during cycling result in severe displacement of silicon particles and structural collapse of electrodes. Here we report the use of a supremely elastic gel polymer electrolyte to address this problem and realize long-term stable cycling of silicon monoxide anodes. The high elasticity of the gel polymer electrolyte is attributed to the use of a unique copolymer consisting of a soft ether domain and a hard cyclic ring domain. Consequently, the displacement of silicon monoxide particles and volume expansion of the electrode were effectively reduced, and the damage caused by electrode cracking is alleviated. A SiO|LiNi₀.₅Co₀.₂Mn₀.₃O₂ cell shows 70.0% capacity retention in 350 cycles with a commercial-level reversible capacity of 3.0 mAh cm⁻² and an average Coulombic efficiency of 99.9%.
Rechargeable lithium (Li)-ion batteries have been widely used in portable electronics, electric vehicles, and grid energy storage devices. To increase the battery energy density, great efforts have been devoted to the development of high-capacity anode materials. Silicon (Si)-based materials are extremely promising owing to their high specific capacities and low operation potentials. Unfortunately, the huge volume changes of Si-based materials result in remarkable displacement of material particles and thickness increase of electrodes in the lithiation process, causing the loss of electrode integrity, unstable solid-electrolyte interphase (SEI) layers, and electrode peeling-off from current collectors. Consequently, the capacity fades quite rapidly, and this problem has become a major obstacle hindering the Si-based anode technology.

Despite the development of various structured Si-based materials and Si-carbon composites, the displacement of material particles and structural collapse at the electrode level remains unsolved, especially when the mass loading of active materials is sufficiently high. To address this problem, different functional binders show the capability of alleviating the particle pulverization and maintaining the electrode integrity. Besides, researchers have recently reported a polyrotaxanes-based polymer and self-healing polymers that can repair the damage and cracks in the electrode and maintain the integrity of micro-sized Si anodes.

In addition to the repair of electrode structure after cracking occurs, strategies to intrinsically alleviating the displacement of material particles and electrode cracking are highly needed. To this end, we here report a strategy using a supremely elastic gel polymer electrolyte (GPE), serving as an intra-electrode cushion to reduce the electrode expansion during lithiation and to facilitate the electrode to recover its structure during delithiation. We demonstrate a copolymer, namely poly(poly(tetramethylene ether) glycol-co-4,4’-methylene diphenyl disiocyanate)-ethylene diamine), enabling reliable electrode structure and stable cycling of micro-sized silicon monoxide (SiO) anodes at high loading conditions. The polymer is uniformly filled in the SiO electrode (Fig. 1b). It contains a soft ether-based domain and a hard cyclic ring-based domain, therefore, presenting excellent elasticity. Meanwhile, the addition of polymers within the electrode has generally deteriorated the Li ion transport. This polymer can uptake liquid electrolyte to form a GPE with an excellent ionic conductivity. Mechanical and morphological studies show that the use of the elastic GPE effectively reduces the absolute displacement of SiO particles and stabilizes electrode structure upon cycling. The severe electrode cracking and the peeling-off of SiO particles from the current collector are suppressed. SiO anodes with the elastic GPE have a reversible specific capacity of 1068 mAh g⁻¹ in 250 cycles. When pairing with a LiNi₀.₅Co₀.₂Mn₀.₃O₂ (NCM) cathode, the cell displays capacity retention of 70.0% in 350 cycles with a reversible capacity of 3.0 mAh cm⁻² and an average Coulombic efficiency of 99.9%.

**Results**

**Chemical and physical properties of the elastic GPE.** We utilized a soft ether-based domain, poly(tetramethylene ether) glycol (PTMG), and a hard cyclic ring-based domain, 4,4’-methylene diphenyl disiocyanate)-ethylendiamine (MDI-EDA), to compose the copolymer for GPE (Supplementary Figs. 1–3). The soft domain can swell in carbonate electrolytes; and the hard domain can prevent excessive swelling of the entire copolymer and has chemical weak interactions (hydrogen bonding and π-π interactions) within the polymer chains. This unique soft-hard combined structure not only provides the copolymer with supreme elasticity but also helps maintain the electrode integrity with cycling. We synthesized three copolymers with different ratios of the soft and hard domains (Fig. 2a) and studied their chemical and physical properties used as GPE.

To compare the performance of the copolymers, we examined the mechanical strength and electrolyte swelling of the copolymers, and cycle life of the SiO electrodes incorporating the copolymers as GPE. The copolymer 1 with a proper MDI-EDA (hard)-PTMG (soft) ratio of 2:1 presents the optimal elongation capability, electrolyte swelling amount, and stabilization of SiO anodes. Figure 2b shows the rubbery property measured by a stress-strain test. The copolymer 1 can tolerate an elongation of above 900% and presents a modulus of 1.2 MPa. Meanwhile, it swelled in a...
Fig. 2 Structural optimization and characterization of the elastic GPE. a Structure of the copolymers, containing a soft domain (PTMG) and a hard domain (MDI-EDA) with different ratios. b Stress-strain curves of the copolymers. c Cycling stability of the SiO electrodes with the copolymers. d Swelling test of the polymer membranes in a 1 M LiPF_6 in EC/DEC electrolyte. e Stress-strain curves of the copolymer 1 before and after swelling. f Peel adhesion of SiO electrodes. The electrode was peeled-off from the Cu current collector using a 90-degree dragging force. g Ionic conductivity measurement of the elastic GPE and liquid electrolyte as a function of temperature.

We further characterized the mechanical properties of the optimal elastic GPE. The GPE showed even better mechanical property than the dry copolymer 1. It tolerated more than 2300% elongation upon stretching before breakdown (Fig. 2e), which is more than twice larger than the copolymer 1. The Young’s modulus of 0.7 MPa, indicating that the GPE remains highly elastic. At the electrode level, the GPE cushion is evenly distributed within the electrode. The as-prepared SiO electrode has a smooth surface (Supplementary Figs. 5, 6). X-ray photoelectron spectroscopy (XPS) analysis indicates a uniform covering of the polymer on the SiO surface, evidenced by the observation of N signals (Supplementary Fig. 7). Meanwhile, we found uniformly distributed N signals throughout the electrode in the cross-sectional energy dispersive X-ray spectrometry (EDS) images (Supplementary Fig. 8). With the elastic GPE, strong adhesion between SiO particles and current collectors was realized, as evidenced by a peel-adhesion test (Fig. 2f). The uncycled SiO electrode with the copolymer has an adhesion strength of 0.4 N, while that of the bare SiO electrode is only...
0.2 N. Furthermore, after vigorously stirring the SiO electrodes in a solvent, we found that the control SiO electrode was seriously damaged as a large amount of SiO particles were peeled off (Supplementary Fig. 9). Surprisingly, the SiO electrode with the copolymer is quite stable, further indicating a strong adhesion. Besides, the elastic GPE displays an ionic conductivity of $2.4 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C, comparable to that of the liquid electrolyte (Fig. 2f and Supplementary Fig. 10). Moreover, cyclic voltammetry studies imply that the GPE is stable in a wide electrochemical window (up to 4.5 V versus Li$^{+}$/Li) (Supplementary Fig. 11).

Structural evolution of SiO electrodes upon cycling. To study the integrity of SiO electrodes upon cycling, we in situ measured the changes in electrode thickness during repeated lithiation and delithiation processes. The initial thicknesses of the electrodes were normalized as 100%. At the beginning of the initial lithiation process, the SiO electrodes with and without the elastic GPE have no obvious changes in the electrode thickness. This is because the electrodes are porous and can accommodate the expansion of SiO particles. Upon lithiation, the electrode thickness began to increase rapidly. The control SiO electrode shows a large thickness increase of 94% (Fig. 3a). Surprisingly, the thickness increase of the SiO electrode with the elastic GPE is only 53%, which is significantly reduced compared to the conventional SiO electrode. In the following delithiation, the electrodes correspondingly shrank. The thickness of the SiO electrode with the elastic GPE was dropped to 120%. The 20% thickness increase of the electrode can be assigned to the formation of the SEI layer, inactive Li$_2$O, and lithium silicate. Contrarily, the control electrode has a 52% thickness increase at the delithiation status, resulting from severe cracking at the electrode level. The SiO electrode with the elastic GPE maintains stable thickness changes in the following cycles, indicating a reliable electrode structure without severe cracking and damage.

We observed the electrode morphology using scanning electron microscopy (SEM) to further investigate the structural integrity of the SiO electrodes. The control SiO electrode presents large cracks only after 10 cycles (Fig. 3b). The cross-sectional SEM image showed large cracks within the electrode, which causes electrode delaminating from current collectors (Fig. 3c). The cracks continued to grow after 20 cycles (Supplementary Fig. 12). In contrast, the SiO electrode with the elastic GPE had much fewer cracks after 10 cycles (Fig. 3d). The cross-sectional SEM image displayed minor cracks and the electrode is very dense (Fig. 3e). This morphology remained after 20 cycles (Supplementary Fig. 12), indicating good reliability of the electrode structure. We also studied the impedance evolution of Li|SiO cells with cycling, the cell incorporating the elastic GPE had stable resistances without a clear increase in 100 cycles, while the resistances of the control sample grew rapidly (Supplementary Fig. 13). Together, all these findings verify the dramatically improved electrode integrity of the SiO electrode during repeated lithiation and delithiation processes.

Interfacial stability of SiO anodes. We next investigated the SEI stability by conducting high-resolution XPS on the surface of SiO electrodes after 10 cycles. In the XPS spectra of a cycled SiO...
Electrochemical performance of SiO anodes. After confirming the electrode integrity, we evaluated the cycling stability of SiO anodes. We optimized the copolymer amount in the electrode. The GPE-incorporated SiO anode had a decreased specific capacity when excessive copolymer was used (Supplementary Fig. 14). The SiO anode with a copolymer amount of 0.4 mg cm$^{-2}$ displayed a decent capacity and rate capability (Supplementary Fig. 15). We also compared the elastic GPE with other polymers used as the cushion, including polyacrylic acid (PAA), polyvinyl alcohol (PVA), PAA-PVA, and poly(vinylidenefluoride-hexafluoropropylene) (PVdF-HFP). These polymers presented poor elasticity and ionic conductivity, resulting in reduced cycling stability and large polarization of SiO anodes (Supplementary Fig. 16). It is also noted that to use the copolymer as additional binders showed no improvements on the SiO anode stability (Supplementary Fig. 17). These findings indicate the importance of using a highly elastic GPE as the cushion.

We next tested the cycling stability of SiO|NCM full cells. To compensate for the irreversible loss of active Li, the SiO anodes were pre-cycled for 1 cycle and displayed a reversible capacity of 4.0 mAh cm$^{-2}$. Then the SiO anodes were paired with fresh NCM cathodes (3.4 mAh cm$^{-2}$). The cell incorporating the elastic GPE had an initial charge capacity of 3.5 mAh cm$^{-2}$ and an initial discharge capacity of 3.0 mAh cm$^{-2}$. A capacity retention of 70.0% in 350 cycles was achieved (Fig. 5a), associated with limited cell polarization (Fig. 5b). In contrast, the control cell presented capacity retention of merely 70.0% in 76 cycles and had severe polarization (Fig. 5c). We calculated the Coulombic efficiency-cycle life relationship (Supplementary Fig. 18) and found that it is pivotal to reach a Coulombic efficiency of 99.9% for Si-based anodes in order to realize a capacity retention of 80% in 225 cycles, which is promising for practical use$^{48,49}$. The use of the highly elastic GPE enabled a Coulombic efficiency of 99.9% in 300 cycles. Note that the use of the elastic GPE stabilized the micro-sized Si electrode as well (Supplementary Fig. 19).

Discussion
In this work, we report a supremely elastic gel polymer electrolyte that intrinsically alleviates the damage and cracking of Si-based anodes at the electrode level. This involves the use of a unique copolymer containing soft and hard domains. The increase of electrode thickness and the displacement of SiO particles were effectively reduced, realizing a reliable electrode structure upon cycling. Significantly improved cycle life and efficiency of SiO|NCM 523 cells were achieved at high-capacity conditions. Using the approach demonstrated in this work, more functional GPEs can be designed for practical high-performance Si-based anodes.
polypyrrolidone (Sigma-Aldrich) at a mass ratio of 90:5:5 in N-methyl-2-pyrrolidone (Sigma-Aldrich) to form slurry. The solid content of the slurry was ~45 wt%. After casting the solution on an aluminum foil, the electrode was dried at 100 °C under vacuum for 12 h. The mass loading of NCM 523 active material was 20 mg cm⁻².

Electrochemical tests. Half-cell tests were performed in a CR 2016 type coin cell assembled with Li metal (250 μm) as the counter electrode. The electrolyte was 1 M LiPF₆ in EC/DEC (v/v 1:1, BASF) with 10 w/o fluorobenzene carbonate (FEC, BASF) additive. Galvanostatic cycling test was carried out at 0.3 mA cm⁻² for the first cycle and 1.0 mA cm⁻² for the rest cycles between 0.01 V and 1.5 V on a BT2000 battery testing system (Arbin Instruments, USA). The specific capacity was calculated on the SiO active material. For full-cell tests, the SiO anodes were pre-charged and pre-discharged for one cycle with a current density of 0.3 mA cm⁻². The pre-cycled SiO electrodes with a mass loading of 4.7 mg cm⁻² and a reversible capacity of 4.0 mA h cm⁻² were paired with NCM cathodes (mass loading of 20 mg cm⁻², reversible capacity of 3.4 mA h cm⁻²) with an N/P ratio of 1.18. The full cell was cycled between 2.8 and 4.2 V at a small current density of 0.3 mA cm⁻² for 3 cycles and then cycled at 1.0 mA cm⁻² under a constant current–constant voltage mode. At the end of each charge cycle, the cell was held at 4.2 V until the current density drops below 0.3 mA cm⁻². To conduct the swelling test, the polymer membrane was cut into a round disk (40 mg, 12 mm in diameter and 500 μm in thickness) and then immersed in a 1 M LiPF₆ in EC/DEC (v/v 1:1, BASF) electrolyte and charged at 0.1 C rate. The membrane weights were measured after various time periods. To measure the ionic conductivity, the saturated membrane was assembled in a coin cell with two stainless steel spacers as working and counter electrode, respectively. The ionic conductivity was measured as a function of temperature using electrochemical impedance spectroscopy (0.1 Hz–10¹² Hz). For the cyclic voltammetry test, the polymer membrane was sandwiched between a stainless steel working electrode and a Li metal counter electrode in a coin cell. The cell was cycled between −0.2 and 4.6 V at a scan rate of 0.2 mV s⁻¹.

In situ electrode thickness method. The SiO anode electrode was assembled into an HS Swell Analysis Cell from Hoshen Corp in a glove box. After assembly, the test cell was removed from the glove box and placed in the test cell stand that holds a Maccor battery tester 4000. The change in electrode thickness every thirty seconds was recorded while the test cell was charging and discharging.

Characterizations. Fourier-transform infrared spectroscopy (FT-IR) was performed using a Bruker IFS 66/S FT-IR spectrometer and Spectra-Tech Collector II DRIFT accessory. The electrochemical impedance and cyclic voltammetry were tested in Solartron 1260 equipment. X-ray photoelectron spectroscopy (XPS) was conducted with a Kratos Analytical Axis Ultra XPS using an air-sensitive holder. The change in electrode thickness every thirty seconds was recorded while the test cell was charging and discharging.

Data availability. The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Author contributions
Q.H., J.S. and Do.W. conceived the ideas. Q.H. and Do.W. designed the experiments. A.G. and Do.W. directed the project. Q.H. performed the material synthesis, characterization, and swelling experiment of the GPE. S.P. and C.U. performed the mechanical test and in situ electrode thickness change work. Q.H. and J.S. performed the EIS test and battery tests. Y.G., Da.W., and S.L. performed the XPS and SEM tests. All authors discussed and analyzed the data. Q.H. and Do.W. wrote the paper.

Competing interests
The authors declare no competing interests.

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