Supporting Information

Revealing the Overlithiation Effect on Cycling and Calendar Aging of the Silicon/Graphite Electrode for High-Energy Lithium-Ion Batteries

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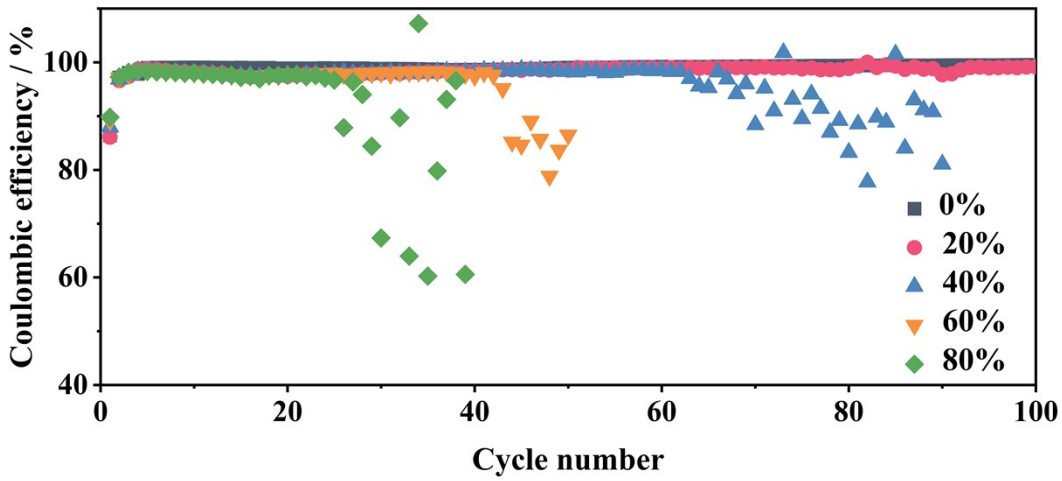

Figure S1. Coulombic efficiency of Si/Gr electrodes with different overlithiation degrees.

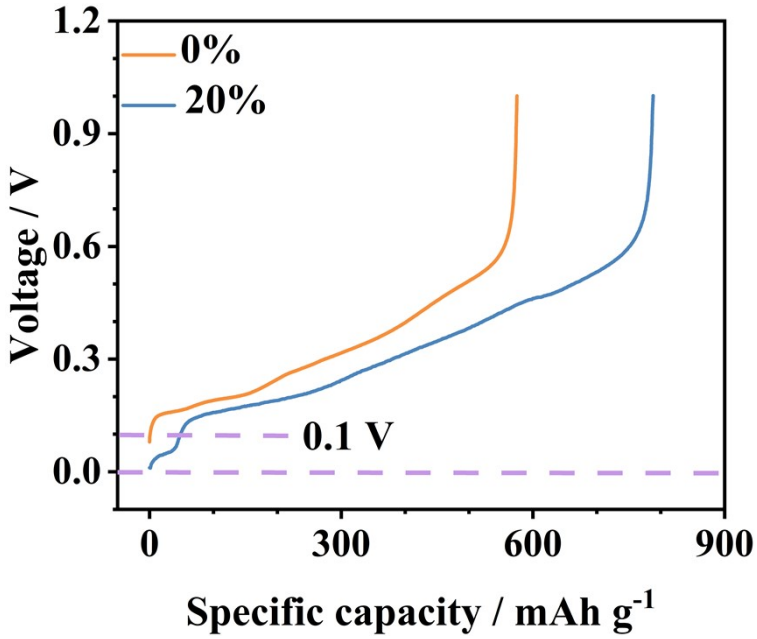

Figure S2. Charge curves of Si-OL-0% and Si-OL-20% electrodes for the 100th cycle.

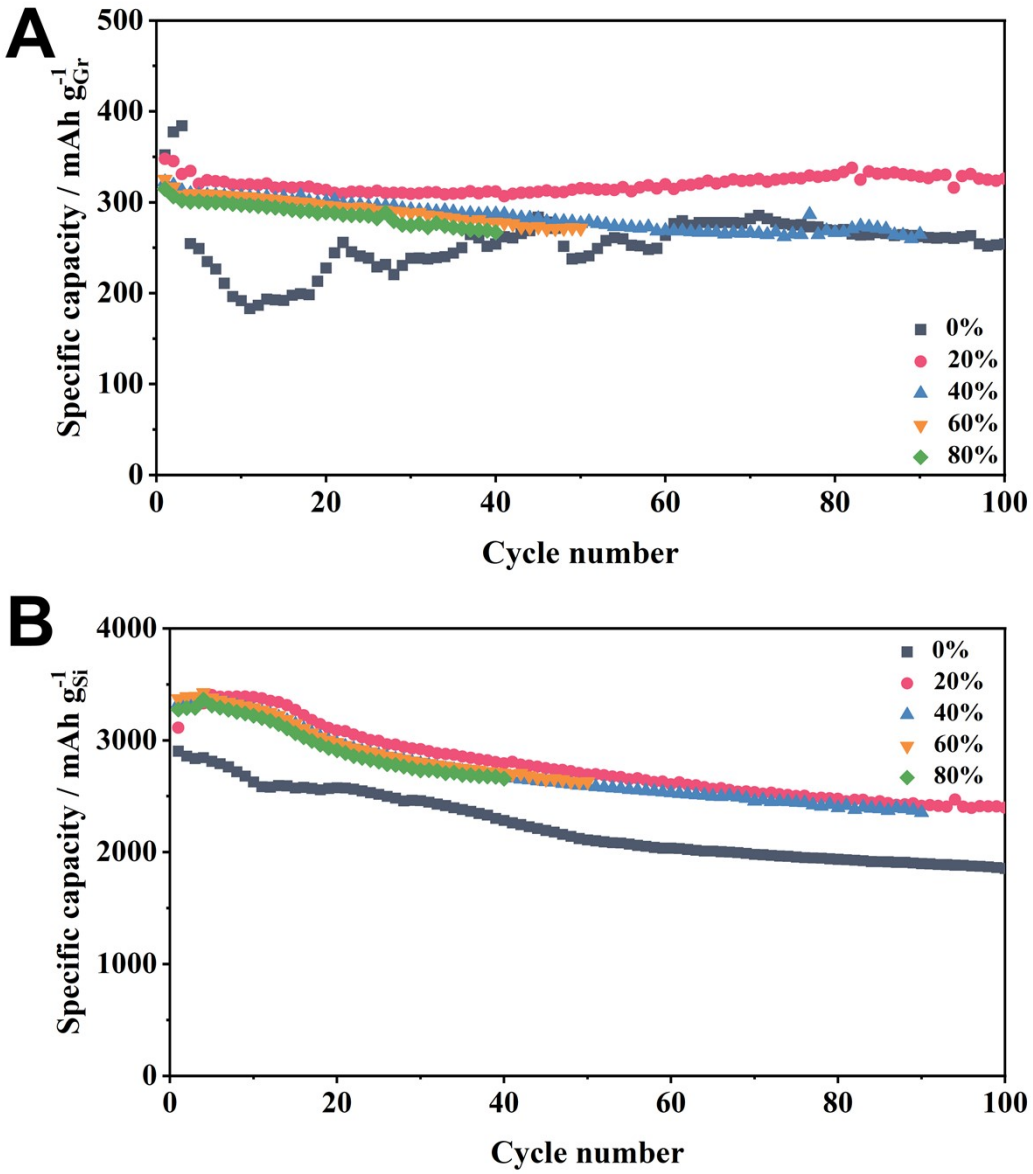

Figure S3. Reversible delithiation capacities of (A) Gr and (B) Si in Si/Gr electrodes with overlithiation degrees of 0%, 20%, 40%, 60% and 80%.

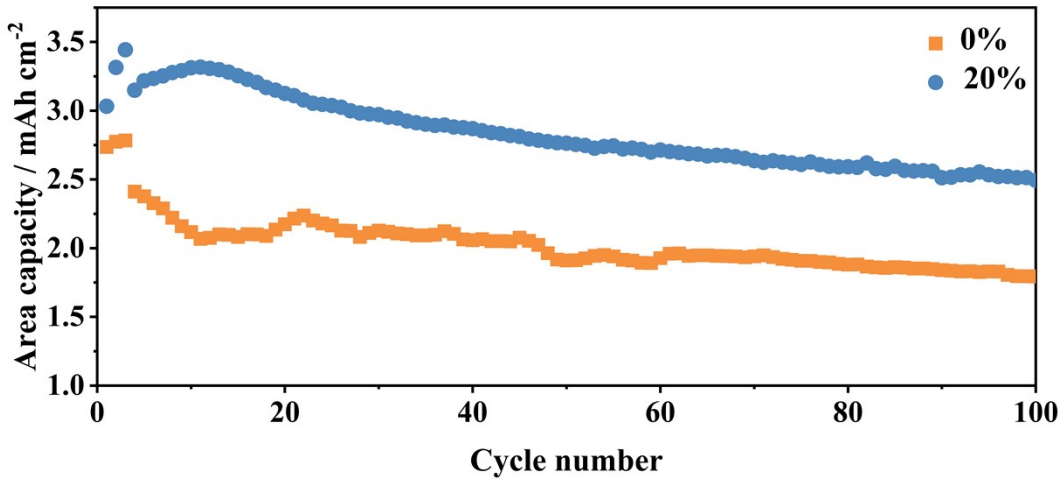

Figure S4. Area capacities of the Si/Gr-OL-0% and Si/Gr-OL-20% electrodes.

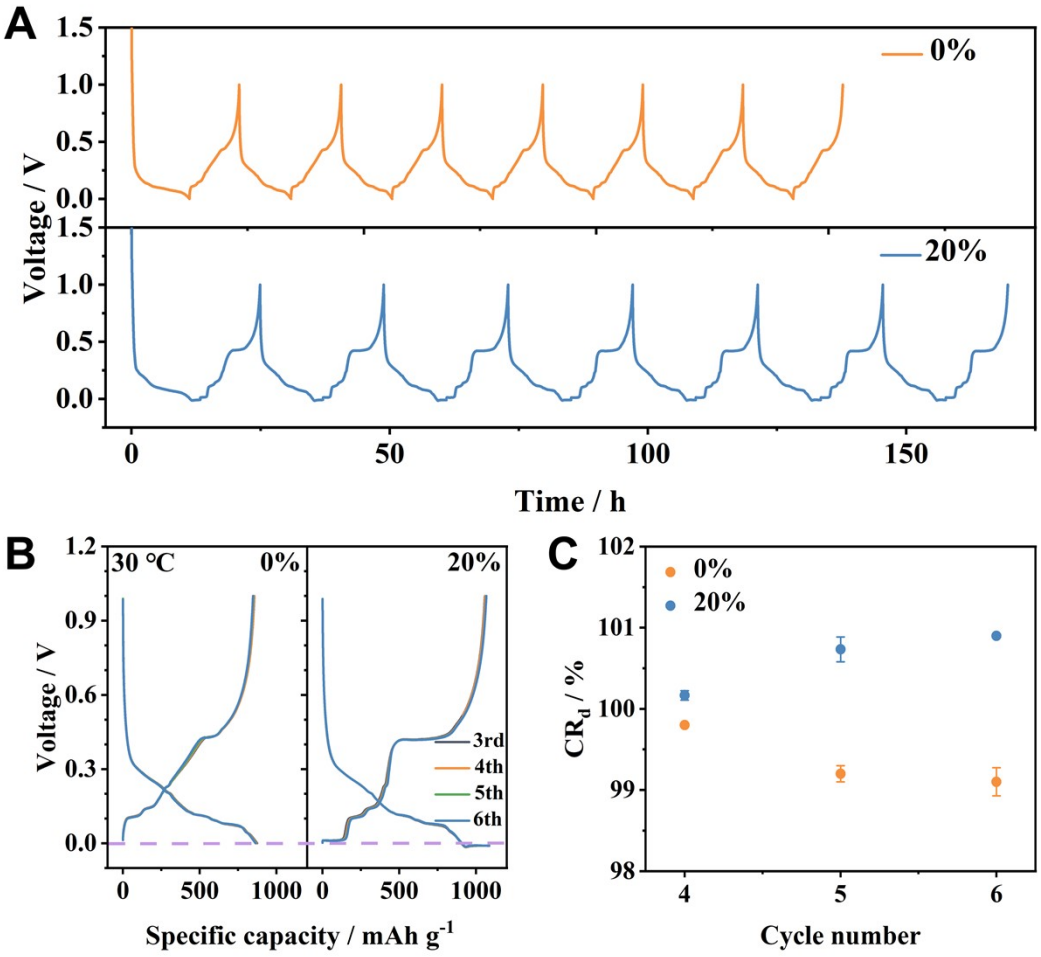

Figure S5. Electrochemical behaviours of Si/Gr-OL-0% and Si/Gr-OL-20% electrodes without calendar aging. (A) Voltage variations over time, (B) charge-discharge curves for the 3rd, 4th, 5th, and 6th cycles, and (C) capacity retention of Si/Gr-OL-0% and Si/Gr-OL-20% electrodes.

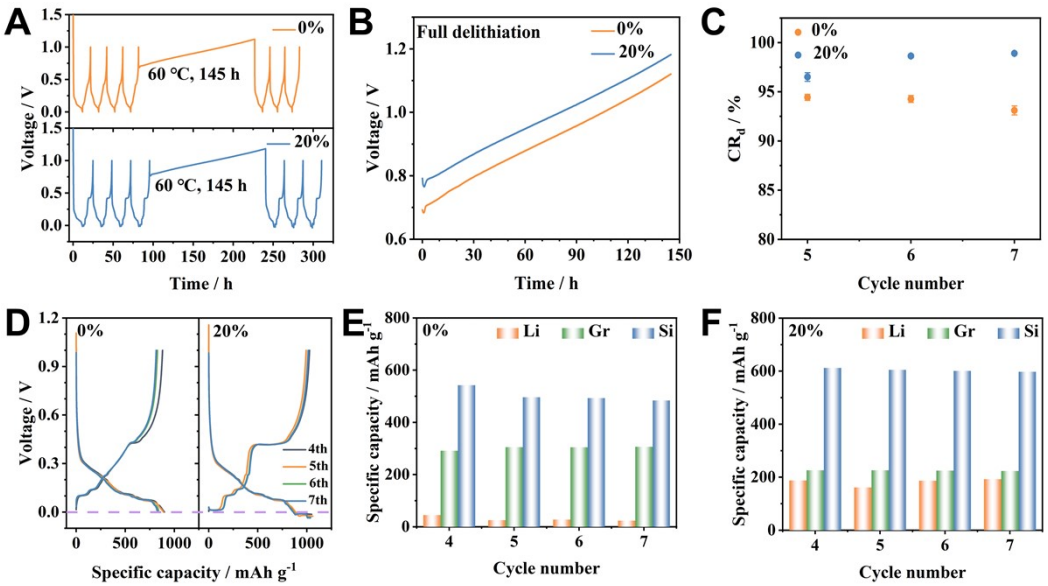

Figure S6. Effect of overlithiation on fully delithiated Si/Gr-OL-0% and Si/Gr-OL-20% electrodes with calendar aging at 60 °C. (A) Voltage variations, (B) time-dependent voltage profiles, (C) capacity retention, and (D) voltage-capacity curves of delithiated Si/Gr-OL-0% and Si/Gr-OL-20% electrodes. Fluctuations in Li stripping, Gr deintercalation, and Si dealloying capacities of delithiated (E) Si/Gr-OL-0% and (F) Si/Gr-OL-20% electrodes before and after the aging process.

The fully delithiated Si/Gr electrodes were maintained at 60 °C for 145 h (Figure S6A). The Si/Gr-OL-20% electrode demonstrates a smaller variation in open-circuit voltage (OCV) of 0.39 V compared to 0.4281 V in Si/Gr-OL-0%. (Figure S6B). The 4th–7th cycles are chosen to probe the impact of calendar aging on the capacity evolution of fully delithiated Si/Gr electrodes. Capacity retention in this scenario is assessed with the equation $CR_{dn} = (C_{dn}/C_{d4}) \times 100\%$. The capacity retentions of Si/Gr-OL-0% electrode in the 5th, 6th, and 7th cycles are 94.4%, 94.3%, and 93.1%, respectively. The overall delithiation capacity displays a remarkable decrease in the 5th cycle, followed by a stabilization in the 6th and 7th cycles, suggesting that the prominent capacity reduction associated with calendar aging is largely irreversible. The deintercalation capacity of Gr (0.1–0.25 V) exhibits marginal changes, while the dealloying capacity of Si (0.25–1.0 V) decreases from 542.4 mAh g^{-1} in the 4th cycle to 496.5 mAh g^{-1} in the 5th cycle and 493.3 mAh g^{-1} in the 6th cycle (Figure 6E). The predominant irreversible loss is attributed to the deactivation of Si particles. For the Si/Gr-OL-20% electrode, a decline is also found in the 5th cycle. Unlike the Si/Gr-OL-0% electrode, the delithiation capacity partially recovers in subsequent cycles. The retentions of the Si/Gr-OL-20% electrode in the 5th, 6th, and 7th cycles are 96.5%, 98.6%, and 98.9%, respectively. Detailed analysis of segmented capacity for the Si/Gr-OL-20% electrode reveals that the Li stripping capacities during the 4th to 7th cycles are 188, 161.4, 186.9 and 192.9 mAh g^{-1}, respectively. Meanwhile, the corresponding Si dealloying capacities (0.25–1.0 V) are recorded at 612.3, 605.3, 601.2 and 597.8 mAh g^{-1} (Figure S6F). The capacity reduction in the Si/Gr-OL-20% electrode is attributed to the dissolution of Li metal, which is generally recoverable, coupled with

the inactivity of some Si particles, leading to permanent degradation.

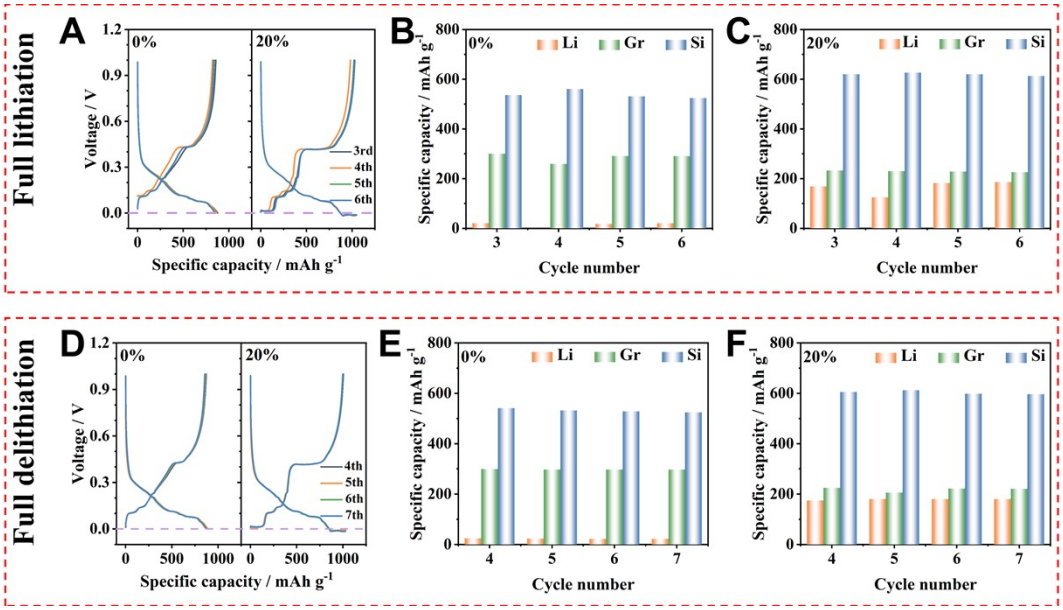

Figure S7. Effect of overlithiation on lithiated/delithiated Si/Gr electrodes during calendar aging at 30 °C for 145 h. Voltage-capacity curves of (A) lithiated and (D) delithiated Si/Gr-OL-0% and Si/Gr-OL-20% electrodes before and after the aging process. Fluctuations in Li, Gr, and Si capacities of lithiated (B) Si/Gr-OL-0% and (C) Si/Gr-OL-20% electrodes, and of delithiated (E) Si/Gr-OL-0% and (F) Si/Gr-OL-20% electrodes before and after aging.

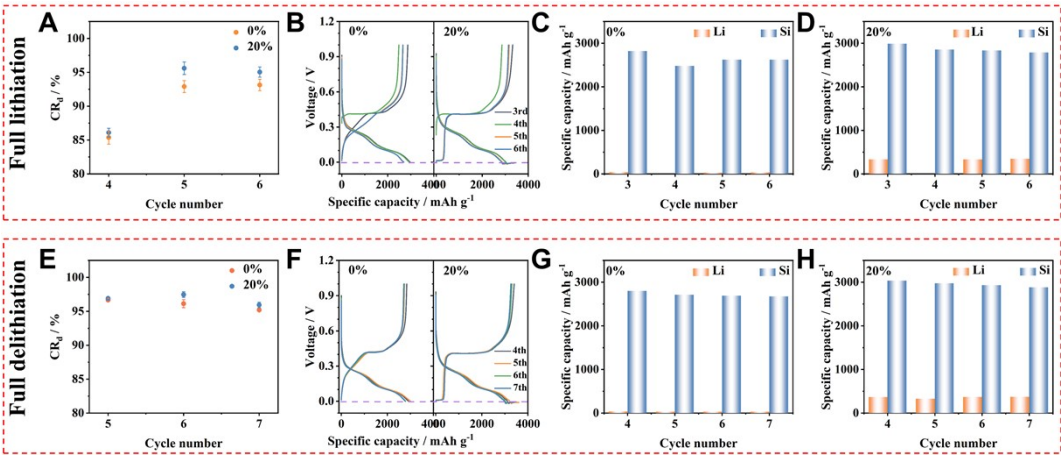

Figure S8. Influence of overlithiation on the capacity retention and electrochemical behaviours of the Si-OL-0% and Si-OL-20% electrodes subjected to calendar aging at 60 °C for 145 h. Capacity retention of the (A) lithiated and (E) delithiated Si-OL-0% and Si-OL-20% electrodes after calendar aging. Charge-discharge curves of the Si-OL-0% and Si-OL-20% electrodes before and after aging at (B) lithiation and (F) delithiation states. Variations in Li and Si capacities of the lithiated (C) Si-OL-0% and (D) Si-OL-20% electrodes, and of the delithiated (G) Si-OL-0% and (H) Si-OL-20% electrodes before and after aging.

The fully lithiated/delithiated pure Si electrode (without Gr) were subjected to calendar aging at 60 °C for 145 h (Figure S8). The aging treatment protocol applied to the Si electrode was identical to that used for the Si/Gr electrode. The Si electrode with a 20% overlithiation degree (marked as the Si-OL-20% electrode) was discharged beyond 0 V to attain a targeted capacity of 400 mAh g^{-1} (20% of 1 *C*, 1 *C* = 2000 mAh g^{-1} for the Si electrode). In contrast, the Si electrode with a 0% overlithiation degree (designated as the Si-OL-0% electrode) was discharged to 0 V. After calendar aging, the capacity retention of the lithiated Si-OL-0% electrode varies from 85.4% in the 4th cycle to 92.9% in the 5th cycle and 93.1% in the 6th cycle (Figure S8A), which is lower than that of the lithiated Si-OL-20% electrode at 86.1%, 95.6%, and 95.0% (Figure S8E), respectively. In the voltage range of 0.1–1.0 V, the Si-OL-0% electrode delivers a decrease from 2824.1 in the 3rd cycle to 2480.6 mAh g^{-1} in the 4th cycle, with a subsequent recovery to 2622.4 mAh g^{-1} in the 5th cycle (Figure S8C). The lithiated Si-OL-20% electrode exhibits Li stripping capacities (< 0.1 V) of 334.3, 0, and 335.2 mAh g^{-1}, along with dealloying capacities of 2989.3, 2857.7, and 2836.4 mAh g^{-1} across the 3rd to 5th cycles (Figure S8D). The dissolution of Li metal could be a primary contributor to the reversible capacity loss. In a full delithiation state, the Si-OL-20% electrode demonstrates a slightly higher capacity retention than the Si-OL-0% electrode (Figure S8E). The Li stripping capacity remains an important factor influencing the overall capacity variation, which changes from 365.9 mAh g^{-1} in the 4th cycle to 327.8 mAh g^{-1} in the 5th cycle and recovers to 369 mAh g^{-1} in the 6th cycle.

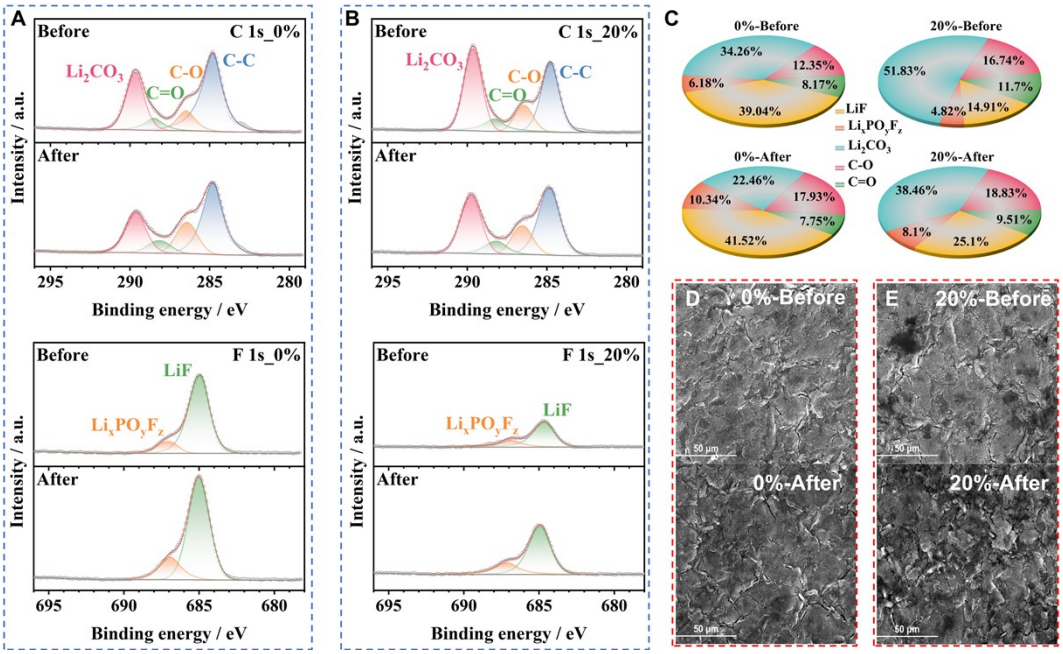

Figure S9. High-resolution C 1s and F 1s XPS spectra of the delithiated (A) Si/Gr-OL-0% and (B) Si/Gr-OL-20% electrodes before and after calendar aging. (C) Corresponding variations in normalized relative contents of organic and inorganic components according to the XPS results. SEM images of the delithiated (D) Si/Gr-OL-0% and Si/Gr-OL-20% electrodes before and after calendar aging.

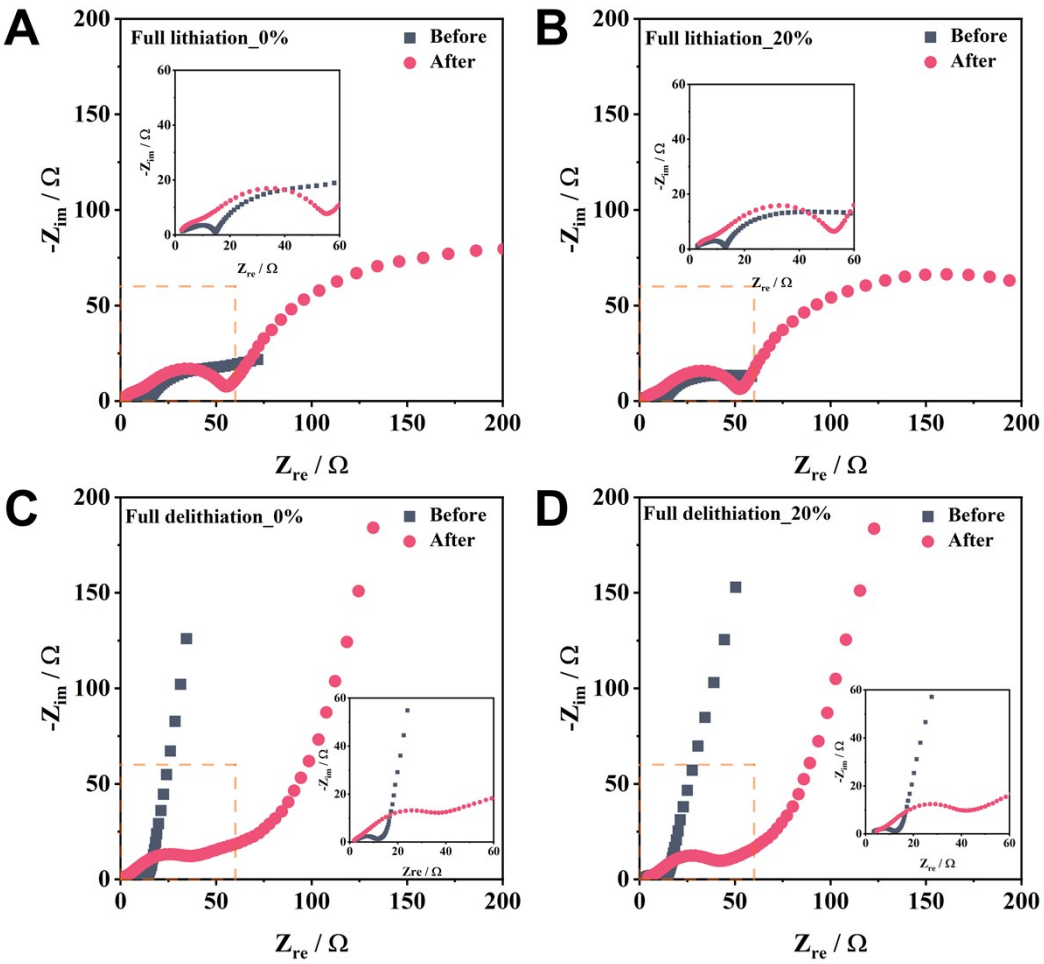

Figure S10. Nyquist plots of the fully lithiated (A) Si/Gr-OL-0% and (B) Si/Gr-OL-20% electrodes before and after calendar aging at 60 °C. Nyquist plots of the fully delithiated (C) Si/Gr-OL-0% and (D) Si/Gr-OL-20% electrodes before and after calendar aging at 60 °C.