

Phase-selective SEI formation dynamics in Si-graphite composite electrodes

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Abstract

Understanding how each phase within a silicon (Si)–graphite composite anode forms its solid–electrolyte interphase (SEI) is essential for advancing interphase engineering in next-generation lithium-ion batteries. However, this question has remained unresolved because conventional electrochemical measurements provide only a volume-averaged response that obscures the contributions of individual phases. Here, by combining phase-resolved operando current measurements with complementary surface-sensitive analyses — X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and scanning spreading resistance microscopy (SSRM) — we reveal that SEI formation in Si–graphite composites is inherently phase-selective. Fluoroethylene carbonate (FEC) decomposes predominantly on Si, producing a fluorine-rich and highly resistive interphase, whereas the graphite surface remains weakly passivated. This imbalance is not a trivial consequence of surface-area differences but arises from the stronger interaction of Si surfaces with electrolyte molecules, as supported by density functional theory (DFT) calculations. The resulting passivation asymmetry highlights a fundamental constraint on interphase engineering in composite electrodes: the SEI on each phase must be optimized through a phase-resolved approach. Importantly, we show that this intrinsic phase selectivity can be turned into a design advantage rather than merely mitigated. As a proof of concept, we employ a co-additive strategy using FEC and vinylene carbonate (VC). Because both additives preferentially reduce on Si, their concurrent decomposition rapidly passivates the Si surface; once this passivation suppresses further additive reduction on Si, the reduction current redistributes toward graphite, ultimately producing a compositionally uniform interphase — both fluorine-rich and polymer-rich — across both phases. This uniform interphase effectively suppresses Li-inventory loss during calendar aging. Our findings establish phase-selective SEI formation as an intrinsic characteristic of composite electrodes and demonstrate that this selectivity can be exploited as a design principle for phase-resolved interphase engineering in multicomponent battery electrodes.

1. Introduction

Silicon (Si)–graphite composite anodes are among the most promising architectures for advancing the energy density of lithium-ion batteries (LIBs), as they combine the high theoretical capacity of Si (3579 mAh g⁻¹ for Li₁₅Si₄) with the proven cycling stability of graphite.¹⁻¹² However, Si and graphite are electrochemically dissimilar materials: they possess different thermodynamic (de)lithiation potentials, operate in overlapping yet distinct potential windows, exhibit markedly different lithiation/delithiation kinetics, and undergo disparate volumetric changes during cycling.^{4,13,14} These differences make the reaction dynamics within the composite inherently complex — (de)lithiation does not proceed uniformly across the two phases, but is instead governed by a continuously shifting interplay of thermodynamic driving forces and kinetic limitations that redistribute current between Si and graphite in a potential-dependent manner.^{4,13}

This complexity in bulk reaction dynamics extends naturally to interfacial processes. The solid–electrolyte interphase (SEI), whose composition, uniformity, and mechanical integrity govern the long-

term reversibility of the anode,^{10-12,15-19} is formed through electrochemical reduction of electrolyte components at the electrode surface.^{10-12,15-19} Because the driving force for such reduction depends on the surface chemistry and electronic structure of the underlying active material, the two phases in a composite electrode are expected to interact differently with the same electrolyte – consuming different species, at different rates, and producing chemically distinct interphases. Moreover, when these two materials coexist within a single composite electrode, they compete for a shared pool of electrolyte species – a competition that can fundamentally alter the interphase that forms on each phase relative to what it would develop as a single-component electrode. In other words, the same thermodynamic and kinetic asymmetry that governs bulk reaction should also make SEI formation inherently phase-selective, not merely different on each phase but coupled through competitive electrolyte consumption. This raises a central question: *in a composite electrode where Si and graphite coexist, how does each phase develop its interphase, and what are the consequences for overall electrode stability?*

Answering this question has proven difficult. Previous studies have extensively characterized SEI chemistry on single-component Si or graphite electrodes using ex situ spectroscopic and microscopic techniques, providing valuable insight into the decomposition products of individual electrolyte additives such as fluoroethylene carbonate (FEC).²⁰⁻²⁸ Yet these single-material investigations cannot capture how Si and graphite interact when they coexist in a functioning composite – a setting in which competitive electrolyte consumption may fundamentally alter the SEI that forms on each phase. Conventional electrochemical measurements on composite electrodes likewise yield only a volume-averaged response, obscuring the contributions of individual phases. As a result, whether SEI formation in composites is truly phase-selective, and if so, to what extent, has remained an open question.

To address this challenge, we combine operando phase-resolved current measurements – obtained using a reaction dynamics analysis (RDA) platform that decouples the electrochemical contributions of Si and graphite within a single cell^{4,29} – with complementary surface-sensitive techniques (XPS, ToF-SIMS, SSRM) and DFT calculations. While previous studies employed the RDA platform to analyze bulk (de)lithiation dynamics,^{4,29} the present work addresses a fundamentally different process: the interfacial decomposition of electrolyte species during SEI formation. This multi-technique approach reveals that SEI formation in Si–graphite composites is markedly phase-selective: FEC, a widely used electrolyte additive,^{20,22,23,28,30-36} decomposes predominantly on Si, generating a fluorine-rich and highly resistive interphase, while graphite remains comparatively weakly passivated. This imbalance reveals a fundamental constraint on interphase engineering in composite electrodes: the SEI on each phase must be optimized through a phase-resolved approach to interphase design. Guided by this principle, we show that the intrinsic phase-selectivity need not be suppressed but can instead be exploited as a design lever. As a proof of concept, we demonstrate a co-additive strategy in which FEC and vinylene carbonate (VC) are co-employed: because both additives preferentially decompose on Si, their concurrent reduction rapidly passivates the Si surface, after which additive decomposition shifts toward graphite, yielding uniform passivation on both phases and suppressing Li-inventory loss during calendar aging.

Beyond the Si–graphite system, the underlying principle — that coexisting phases with distinct surface chemistries and electrochemical potentials drive asymmetric electrolyte decomposition — applies to any composite electrode in which dissimilar materials share a common electrolyte. Blended cathodes (e.g., $\text{LiFePO}_4/\text{LiNiO}_2$) and bimodal layered oxide cathodes (e.g., $\text{LiNi}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.3}\text{O}_2$) composed of large and small particles of identical composition are equally subject to this phenomenon, as supported by preliminary evidence presented in Supplementary Note I. These findings establish phase-selective interphase formation as a general characteristic of composite electrodes. These findings reveal that competitive interfacial reactions between coexisting phases govern SEI formation in composite electrodes, establishing phase-resolved interphase engineering as a guiding principle for multicomponent battery systems.

2. Results

2.1. Different SEI depending on the anode materials chemistry

We prepared three half-cells containing a graphite electrode (Gr_cell), a Si electrode (Si_cell), or a Si–graphite composite electrode with 10 wt. % Si (Si10_cell). All cells employed an FEC-containing electrolyte (10 vol. % FEC) and were lithiated at 0.033 C. After lithiation, the electrodes were harvested and denoted as Gr_W.FEC, Si_W.FEC, and Si10_W.FEC. Ex situ XPS was performed on the C 1s and F 1s core levels (Fig. 1a–b), and the quantitative distributions are summarized in Fig. 1c and Table S1.

Despite identical electrolyte conditions, the two single-component electrodes produced markedly different SEIs. Gr_W.FEC exhibited an F-ratio of 50.9%, with roughly half of the detected surface species being fluorine-related, whereas Si_W.FEC showed a significantly lower F-ratio of 32.3% accompanied by a correspondingly higher proportion of organic carbon species. The carbon-related components also exhibited distinct distributions depending on the electrode chemistry. These contrasting compositions indicate that the electrode surface chemistry governs how the electrolyte is consumed and what interphase is built — even when the available electrolyte is the same.

Remarkably, the composite electrode (Si10_W.FEC) did not exhibit an intermediate SEI between those of its constituent phases. Instead, its F-ratio (18.2%) fell below that of either single-component electrode, and its LiF content (9.1%) was less than half of the values observed for Gr_W.FEC (26.9%) and Si_W.FEC (27.0%). This result suggests that the coexistence of Si and graphite within a single electrode alters SEI formation in a manner that cannot be predicted from each phase alone — motivating a direct, phase-resolved investigation of SEI formation dynamics within the composite, which we undertake using the RDA platform in the following section.

2.2. RDA cell design and validation

Resolving the SEI formation dynamics of each phase within a composite electrode requires decoupling the electrochemical contributions of Si and graphite — a task that conventional measurements cannot

achieve. To address this challenge, we developed a model-electrochemical cell and analysis system, termed the RDA cell, as previously introduced in our group's publications.^{4,29}

In conventional composite electrodes, Si and graphite are electronically connected either directly (via particle-to-particle contact) or through conductive carbon, which can be thermodynamically modeled as two single-component electrodes connected by a low-resistance pathway. To emulate this configuration, we designed a model cell using a standard coin-cell format, as schematically illustrated in Fig. 2a. Additional methodological details are provided in the Methods section or the referenced publications.^{4,29}

This setup allows the total current (I_{total}) supplied by the potentiostat to be distributed between two separate working electrodes — WE_{Si} and $\text{WE}_{\text{Graphite}}$ — depending on the relative electrochemical activity of Si and graphite. For example, during SEI formation, if the reaction predominantly occurs on Si, the current flowing through WE_{Si} (I_{Si}) will exceed that through $\text{WE}_{\text{Graphite}}$ (I_{Graphite}). By placing an ammeter between the two electrodes, we can accurately measure the current through each electrode in real time, enabling direct monitoring of the reaction dynamics of individual components within a single composite electrode during SEI formation.

Given the structural and configurational differences between the RDA cell and a conventional coin-cell, we first validated the reliability of the RDA cell and its associated analysis system. To replicate the electrochemical behavior of the Si10_cell, we prepared two separate working electrodes composed of individual materials: WE_{Si} and $\text{WE}_{\text{Graphite}}$. The weight ratio of Si in WE_{Si} to graphite in $\text{WE}_{\text{Graphite}}$ was fixed at 10:90 to match the composition of the composite electrode. This RDA cell is hereafter referred to as the Si10_R_cell.

The voltage vs. capacity and differential capacity (dQ/dV) vs. voltage profiles for the initial cycle at a C-rate of 0.033 are shown in Fig. 2b–g for both the Si10_R_cell (red) and Si10_cell (conventional coin-cell, black). Data are presented for electrolytes both without the FEC additive (W.O.FEC) and with the FEC additive (W.FEC). The voltage profiles and dQ/dV curves — including several reductive peaks in the higher voltage region corresponding to SEI formation — exhibited strong consistency between the two setups, validating the reliability of the RDA cell for analyzing SEI formation dynamics in composite electrodes.

In the W.O.FEC condition (Fig. 2c–d), a prominent reductive peak was observed at approximately 0.8 V (red-shaded region), attributed to the decomposition of the ethylene carbonate (EC) solvent. In contrast, under the W.FEC condition (Fig. 2f–g), additional reductive peaks appeared around 1.1–1.5 V (blue-shaded region), corresponding to the decomposition of the FEC additive. Furthermore, the reductive peak associated with EC decomposition was significantly suppressed in the presence of FEC, consistent with prior reports indicating that FEC decomposition alleviates EC solvent breakdown.^{28,34–36}

The close correspondence between the RDA cell and the conventional coin-cell across both electrolyte conditions confirms that the RDA platform reliably reproduces the electrochemical behavior of the composite electrode while providing the additional capability of phase-resolved current measurement. Having established this reliability, we next apply the RDA platform to resolve how each phase contributes to SEI formation within the composite.

2.3. Phase-resolved SEI formation dynamics in the composite

Phase-resolved current measurements reveal that the electrolyte decomposition current is not evenly shared between Si and graphite, even in the absence of FEC. Fig. S1 presents the evolution of I_{Si} and I_{Graphite} as a function of voltage for the Si10_R_cell during SEI formation (first lithiation) at a C-rate of 0.033. The measured current values were converted into effective C-rates (C_{Si} and C_{Graphite}) and plotted against voltage for the W.O.FEC (Fig. 3a) and W.FEC (Fig. 3b) conditions. The applied C-rate (blue line in Fig. 3a–b) represents the theoretical current distribution assuming homogeneous current sharing between Si and graphite. Details on the effective C-rate calculation are provided in the Methods section.

Under the W.O.FEC condition (Fig. 3a), C_{Si} substantially exceeds both C_{Graphite} and the applied C-rate within the EC decomposition region (~ 0.8 V, red-shaded), indicating that EC reduction occurs preferentially on Si. This baseline asymmetry becomes far more pronounced when FEC is present. Under the W.FEC condition (Fig. 3b), FEC decomposition is overwhelmingly concentrated on Si: in the FEC reduction region (1.1–1.5 V, blue-shaded), C_{Si} peaks at 0.057 – 6.3 times greater than C_{Graphite} . After the first lithiation, all reductive peaks associated with electrolyte decomposition disappeared in subsequent cycles (Fig. S2). Because Si particles are substantially smaller than graphite particles and therefore expose a much larger specific surface area (Fig. S3 and Table S2), one possible alternative explanation is that the larger decomposition current on Si simply reflects geometric surface-area differences. To test this directly, we normalized the measured currents to particle surface area and compared the resulting current densities with the values expected for uniform current sharing (Fig. S4). Even after this normalization, the current density on WE_{Si} remains higher than the uniform-distribution expectation, whereas that on $\text{WE}_{\text{Graphite}}$ remains lower, demonstrating that the asymmetric reaction is not a trivial consequence of surface-area imbalance alone.

XPS analysis confirms that this asymmetric current distribution translates directly into disparate SEI compositions on the two phases. XPS was performed on WE_{Si} and $\text{WE}_{\text{Graphite}}$ electrodes harvested from Si10_R_cells after the first lithiation under both W.O.FEC and W.FEC conditions (C 1s spectra in Fig. 3c, F 1s spectra in Fig. 3d, quantitative distributions in Fig. 3e and Table S3). The harvested electrodes are denoted as Si_R_W.O.FEC, Si_R_W.FEC, Gr_R_W.O.FEC, and Gr_R_W.FEC, respectively.

The most revealing observation is that FEC leaves only a minor compositional fingerprint on graphite within the composite. Despite the presence of 10 vol. % FEC in the electrolyte, the SEI on graphite (Gr_R_W.FEC) closely resembles that formed without FEC (Gr_R_W.O.FEC): both the F-ratio and the

distribution of surface species show only minimal variation, indicating that FEC decomposition contributes minimally to SEI formation on the graphite surface within the composite.

In sharp contrast, preferential FEC decomposition on Si produces a dramatically different outcome. The F-ratio on Si surges from 11.8 % (Si_R_W.O.FEC) to 49.4 % (Si_R_W.FEC), accompanied by a pronounced increase in LiF content from 10.01% to 30.5 % — indicating the formation of a highly fluorine-rich SEI. Notably, this F-ratio even exceeds that of the single-component Si electrode cycled with FEC (Si_W.FEC, 32.3 % in Fig. 1c), a direct consequence of FEC being preferentially channeled toward Si in the composite rather than being shared between both phases. We note that the F-ratio reflects the relative proportion of fluorine- to carbon-related species rather than the absolute fluorine content; the higher F-ratio on Si_R_W.FEC therefore indicates a compositionally more fluorine-dominated SEI, not necessarily a greater total absolute fluorine content.

ToF-SIMS depth profiling independently corroborates this picture (Fig. 3f–i). The SEI/bulk boundary was defined as the sputtering depth at which the normalized C^- (for graphite) or Si^- (for Si) signal reached 80% of its maximum (Fig. S5). On the graphite side (Fig. 3f–g), the depth profiles of F^- and LiF_2^- for Gr_R_W.FEC closely resemble those of the FEC-free condition (Gr_W.O.FEC) rather than the single-component graphite cycled with FEC (Gr_W.FEC), confirming that FEC-derived fluorine species contribute far less to the graphite SEI in the composite than in the single-component electrode. On the Si side (Fig. 3h–i), the trend is reversed: F^- and LiF_2^- intensities in Si_R_W.FEC are not only higher than in Si_W.O.FEC (single-component Si electrode cycled without FEC) but surpass even Si_W.FEC across the entire SEI depth, consistent with the concentrated FEC decomposition revealed by RDA and XPS.

DFT calculations provide a mechanistic rationale for this preferential decomposition on Si (Fig. 4). Both EC and FEC adsorb more strongly on Si surfaces than on graphite, with the largest adsorption energies found on Si(100): -0.84 eV (EC) and -0.68 eV (FEC), compared with -0.35 and -0.27 eV on graphite zigzag edges, respectively (Fig. 4a–b). Bader charge analysis further reveals that both molecules extract more charge from Si than from graphite in the neutral state, and this trend persists upon introducing additional electrons into the system (Fig. 4c–d). These results indicate that Si surfaces provide both a stronger thermodynamic driving force for adsorption and a greater electron-donating propensity, rationalizing why electrolyte reduction is preferentially initiated on Si. The same trends hold when EC and FEC are coordinated with Li atoms (Fig. S7–S8), indicating that this selectivity is robust across different solvation environments.

Taken together, the operando current analysis, surface-sensitive XPS, depth-resolved ToF-SIMS, and DFT calculations converge on a single conclusion: FEC decomposition in the Si–graphite composite is quantitatively phase-selective, driven by the stronger thermodynamic affinity of Si surfaces for electrolyte molecules. This asymmetry produces a fluorine-rich SEI on Si while leaving graphite with minimal FEC-derived passivation. Importantly, the SEI on each phase in the composite differs markedly from that formed on the corresponding single-component electrode — Si benefits from enhanced fluorine

enrichment, whereas graphite receives substantially less FEC-derived passivation than it would as a single-component electrode.

2.4. The impact of phase-selective FEC decomposition for SEI stability

The preceding sections establish that FEC decomposition in the composite is concentrated on Si, producing chemically distinct SEIs on the two phases. A critical question remains: *does this compositional asymmetry translate into a functional difference in passivation quality?* To answer this, we employed scanning spreading resistance microscopy (SSRM), which provides a spatially resolved measure of electronic resistance across the electrode surface. Higher spreading resistance indicates a more insulating — and thus more effectively passivating — SEI layer.^{12,37-39} Because the intrinsic conductivity of Si and graphite differ substantially, absolute SSRM values are meaningful only for comparisons within the same material class (Si-to-Si or graphite-to-graphite), not across materials.

For single-component electrodes, FEC unambiguously improves passivation. Pristine electrodes exhibited very low resistance (Fig. 5a-1, a-5), which increased after the first lithiation across all samples (Fig. 5a-2–a-8, Fig. 5c–d), confirming SEI formation. Both Gr_W.FEC and Si_W.FEC showed more uniformly elevated resistance than their W.O.FEC counterparts (Fig. 5a-2 vs. a-3, a-6 vs. a-7, Fig. 5c–d), consistent with prior reports on FEC-derived SEI stabilization.^{20,22,23,28,30-36} If FEC were equally effective on both phases within the composite, one would expect a similarly beneficial effect on graphite and Si alike.

Within the composite, however, the passivation outcome is strikingly asymmetric — and for graphite, it is not merely suboptimal but actively worse than when graphite is cycled as a single-component electrode. Si_R_W.FEC exhibits the highest average resistance among all Si samples (Fig. 5d), indicating that the concentrated FEC decomposition produces an exceptionally well-passivated interphase on Si. Conversely, Gr_R_W.FEC shows even lower resistance than the single-component Gr_W.FEC (Fig. 5c). This is a remarkable result: the presence of FEC in the electrolyte not only fails to improve graphite passivation within the composite but yields an outcome worse than what graphite achieves as a single-component electrode under the same electrolyte conditions. The explanation follows directly from the phase-selective decomposition established in Section 2.3 — FEC is predominantly consumed by Si, leaving insufficient FEC-derived species to effectively passivate graphite.

This passivation imbalance underscores that interphase engineering in composite electrodes demands a phase-resolved approach — one that recognizes and addresses the distinct passivation requirements of each phase. We explore this direction in the following section.

2.5. Cooperative SEI design via co-additive saturation

The foregoing analysis reveals a fundamental limitation of single-additive strategies in composite electrodes: because FEC decomposes predominantly on Si, improving passivation on one phase comes directly at the expense of the other. We therefore explored a co-additive strategy in which FEC and

vinylene carbonate (VC) are employed together. VC is one of the most widely adopted SEI-stabilizing additives, known to polymerize upon electrochemical reduction and form mechanically robust polymeric SEI components.⁴⁰⁻⁴³

A prerequisite for understanding the co-additive system is the decomposition behavior of VC itself. RDA analysis of the W.VC condition (10 vol. % VC, without FEC; Fig. S9) reveals that VC decomposition current is also concentrated on Si rather than graphite. This shared Si-preference of both FEC and VC is central to the mechanism discussed below.

Based on this observation, we formulated an electrolyte denoted as W.VC.FEC, containing 5 vol. % VC and 5 vol. % FEC — maintaining the same total additive content (10 vol. %) as the FEC-only condition (W.FEC) to enable a direct comparison. The dQ/dV profiles of the Si10_R_cell under each electrolyte condition (Fig. S10) reveal the decomposition characteristics of each additive. Under the W.FEC condition, FEC reduction onsets near ~1.5 V and exhibits a pronounced high-voltage reduction peak, whereas VC reduction under the W.VC condition shares a similar onset but displays its most pronounced feature near ~1.0 V. The two additives thus decompose over a broadly overlapping voltage window (~1.5–1.0 V), suggesting that when FEC and VC coexist their reduction processes can proceed concurrently rather than in a strictly sequential manner. Strikingly, the co-additive condition (W.VC.FEC) produces a markedly intensified dQ/dV peak immediately following the shared onset near ~1.5 V — substantially exceeding those of the individual additives — pointing to a coupled decomposition process that concentrates a large fraction of the total additive reduction into the earliest stage. The critical question, therefore, is not simply how much decomposition occurs, but how this intensified early-stage reactivity redistributes the decomposition current between the Si and graphite phases.

Phase-resolved current measurements directly address this question (Fig. 6a–b). Under the W.FEC condition, the effective C-rate of Si exhibits a broad current hump near 1.4 V, indicating that the decomposition current remains concentrated on Si over an extended voltage window. When VC is introduced as a co-additive (W.VC.FEC), the overlaid comparison in Fig. 6b reveals a distinctly different profile: Si still captures a large share of the decomposition current initially, but this concentration subsides rapidly, producing a markedly narrower hump. Concurrently, the effective C-rate of graphite rises, indicating that the decomposition current progressively shifts from Si to graphite as the voltage decreases. This redistribution is particularly notable given that both FEC and VC individually exhibit a strong preference for Si — their combined action does not amplify the asymmetry but instead attenuates it.

XPS analysis of the harvested electrodes provides direct compositional confirmation of this more balanced decomposition (Fig. 6c–e). Under the W.VC.FEC condition, the SEI compositions on Si and graphite converge to a striking degree. The F-ratio narrows to 31.0 % (Gr_R_W.VC.FEC) and 30.4 % (Si_R_W.VC.FEC), and the LiF content is likewise comparable. The total fraction of polymeric species (OCOO, C=O, and C–O) — signatures of VC-derived decomposition products^{42,43} — is also nearly identical

on the two phases. This stands in stark contrast to the W.FEC condition, where fluorine was heavily concentrated on Si (F-ratio: 49.4 %) while graphite remained weakly passivated (F-ratio: 13.0 %).

We attribute this counterintuitive convergence to the following mechanism. Because both FEC and VC preferentially adsorb on and reduce at Si surfaces, their concurrent decomposition rapidly builds a resistive interphase on Si. The shape of the Si current hump under the W.VC.FEC condition is consistent with this mechanism: its higher peak intensity reflects the more vigorous co-decomposition of FEC and VC on Si, its rapid rise indicates that this concurrent reduction is initiated promptly, and its sharp decay shows that the resulting interphase quickly suppresses further additive reduction – redirecting the decomposition current toward the comparatively less-passivated graphite surface. This produces a more equitable distribution of decomposition current and, consequently, a compositionally uniform SEI on both phases – opening a distinct passivation pathway that is absent when either additive acts alone.

To verify whether this distinct pathway indeed produces a more resistive interphase on both phases, SSRM analysis was performed (Fig. 7a–c). The average spreading resistance of Gr_R_W.VC.FEC increased substantially compared with Gr_R_W.FEC (Fig. 7b), while Si_R_W.VC.FEC maintained a comparably high resistance, decreasing only marginally from the already well-passivated Si_R_W.FEC level (Fig. 7c). Notably, both phases exhibit high spreading resistance under the co-additive condition: graphite passivation is markedly improved while Si retains its already effective interphase. This result corroborates the XPS findings and confirms that the co-additive strategy achieves effective passivation on both Si and graphite.

Given that calendar aging in Si–graphite composites originates from the persistent reactivity of Si and graphite and their SEIs,^{44,45} which leads to side reactions and Li-inventory loss, the uniformly stabilized SEI achieved by the co-additive strategy is expected to significantly improve calendar life. Accelerated calendar-aging tests were performed on Si10_cells with different electrolyte compositions (W.O.FEC, W.FEC, and W.VC.FEC) in Fig. 7d–g. The cells were first cycled three times at 25 °C at a C-rate of 0.033 C for sufficient SEI formation. Subsequently, they were stored at 45 °C for 3 days, followed by three additional cycles at 25 °C under the same C-rate. This storage–cycling sequence was repeatedly applied.

The Li-inventory loss was quantified from the difference between lithiation and delithiation capacities in each cycle (Fig. 7d–f). After each 3-day storage at 45 °C, a pronounced Li-inventory loss occurred during the first cycle, but the loss was suppressed in subsequent cycles. This trend was consistently observed across all test conditions. A comparison of the Li-inventory loss during the first cycle of each storage set is summarized in Fig. 7g. The largest Li-inventory loss occurred under W.O.FEC due to its unstable SEI. With the addition of FEC alone (W.FEC), the loss was substantially reduced, primarily due to increased SEI stability on Si. When both VC and FEC were co-employed (W.VC.FEC), the Li-inventory loss was further minimized – a result attributable to the uniformly improved SEI stability on both Si and graphite. We also examined cycling performance at 0.2 C (Fig. 7h–i). Both W.FEC and W.VC.FEC cells showed similar capacity retention, both outperforming W.O.FEC.

3. Discussion

A practical implication of this work is that interphase design based on single-material screening may yield misleading conclusions when applied to composite systems. The interphase that each material develops in isolation differs fundamentally from that formed in the presence of a competing phase. In the Si–graphite composite studied here, FEC decomposes predominantly on Si, producing a fluorine-rich SEI that exceeds what Si develops as a single-component electrode, while graphite receives substantially less FEC-derived passivation than it would in isolation. This finding establishes that SEI formation in composite electrodes is not a simple superposition of single-component behaviors but an emergent consequence of competitive interfacial reactions.

Importantly, this phase-selective asymmetry should not be viewed merely as a limitation, but as an intrinsic characteristic of multicomponent electrodes. Because this selectivity originates from fundamental differences in surface adsorption energetics and electron-donating propensity between Si and graphite (Fig. 4), it is expected to persist — albeit with varying magnitude — across different electrolyte formulations and operating conditions. Rather than attempting to eliminate phase selectivity, our results demonstrate that it can be harnessed. In the co-additive system, employed here as a proof-of-concept, the shared preferential reactivity of FEC and VC toward Si accelerates the formation of a resistive interphase on the Si surface. As the Si surface becomes increasingly passivated, further additive reduction on Si is kinetically suppressed, leading to a progressive rebalancing of decomposition current toward graphite and resulting in compositional and functional convergence of the interphase across both phases. This behavior reflects a self-limiting passivation process, in which intrinsic selectivity and kinetic suppression together drive a more balanced distribution of decomposition products.

This perspective reframes interphase engineering in composite electrodes: uniformity need not arise from additive homogeneity, but can emerge from controlled asymmetry followed by kinetic self-limitation. Designing effective interphases therefore requires a phase-resolved understanding of competitive reaction dynamics and strategies that leverage intrinsic selectivity to achieve uniform stabilization.

Notably, the same principle can be applied in the opposite direction. Rather than driving compositional convergence across both phases, additive combinations with complementary — rather than shared — phase preferences could be designed to partition distinct SEI chemistries onto each phase independently. The phase-selective understanding established here thus opens a broader design space for interphase engineering — one in which uniformity and differentiation are both accessible outcomes, depending on the choice of additive combinations and their relative phase affinities.

Beyond Si–graphite anodes, the principle of phase-selective interphase formation is expected to apply wherever compositionally or morphologically distinct phases coexist within a single electrode. Preliminary evidence supports this expectation: RDA and XPS analyses of $\text{LiFePO}_4/\text{LiNiO}_2$ blended

cathodes and $\text{LiNi}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.3}\text{O}_2$ bimodal cathodes (Supplementary Note I) reveal that CEI formation is likewise asymmetric, with LiNiO_2 and polycrystalline-large particles $\text{LiNi}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.3}\text{O}_2$ developing more fluorine-rich interphases than their counterparts. Although these cathode results remain exploratory and warrant dedicated investigation, they indicate that the competitive interfacial framework identified here is unlikely to be unique to the Si–graphite system.

4. Conclusion

This work demonstrates that SEI formation in Si–graphite composite electrodes is governed not by the electrolyte composition alone but by competitive decomposition dynamics between coexisting phases, producing a phase-selective asymmetry. As a result, the SEI in a composite electrode cannot be predicted from single-component studies — a finding with direct implications for how interphases in multicomponent electrodes are characterized, understood, and engineered.

The co-additive strategy introduced here — exploiting, rather than suppressing, the intrinsic phase-selectivity to achieve uniform passivation on both phases — provides a proof of concept for this phase-resolved approach. More broadly, the observation that analogous asymmetries arise in blended and bimodal cathodes suggests that phase-selective interphase formation may be relevant across a wider range of composite electrodes, providing a foundation for phase-resolved interphase engineering in diverse battery chemistries.

5. Methods

Materials: In this study, the particle size of Si was reduced through mechanical crushing using a planetary ball mill. Afterward, Si and graphite powders were combined with a conducting agent and subjected to ball milling for 12 h to ensure homogeneous mixing. The particle-size distribution, determined by particle size analysis (PSA), is shown in Fig. S3. Polyacrylic acid (PAA) served as the binder, while N-methyl-2-pyrrolidone (NMP) was used as the solvent in the subsequent paste-mixing process. The prepared slurries were then coated onto copper current collectors using a doctor-blade technique. The detailed electrode compositions are summarized in Table 1.

Table 1. Composition and characteristics of electrodes consisting of graphite and Si.

		Graphite	Si	Si10
Component, wt. %	Si	-	20	6.5
	Natural graphite	80	-	58.5
	Polyacrylic acid binder	10	10	10
	Super -P	10	70	25
Areal mass loading, mg/cm²		1.0	0.4	0.7
Electrode thickness, μm		18	12	16
Disk size, mm		14	14	14

Cell (dis)assembly and testing: Coin-cells (CR2032) were assembled for all electrochemical measurements and evaluated using a SINOPRO MRX CT-4008T battery tester. A Celgard® 2400 membrane served as the separator and was punched into disks with a diameter of 19 mm. Lithium metal foil (450 μm thickness, 16 mm diameter) was used as the counter/reference electrode. The foil corresponds to 93 mAh/cm² (187 mAh total), ensuring large excess lithium for all half-cell tests. Prior to assembly, the electrodes for electrochemical analysis were vacuum-dried at 110 °C for 12 hours. The electrolyte composition consisted of 1.2 M lithium hexafluorophosphate (LiPF₆) dissolved in a 3:7 (by volume) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC), sourced from Dongwha Electrolyte. For additive-containing electrolytes, FEC and/or VC were added at the concentrations specified in the main text (10 vol. % FEC for the W.FEC condition; 5 vol. % VC + 5 vol. % FEC for the W.VC.FEC condition; 10 vol. % VC for the W.VC condition). All additive concentrations reported in this study are given in volume percent. For each cell, 100 μL of the electrolyte was added. Electrochemical tests were conducted at 25 °C, except for the 45 °C storage condition used in the accelerated calendar-aging test.

All electrochemical tests were conducted within a voltage range of 0.01–1.5 V (vs. Li⁺/Li). The formation process, including the first lithiation process, consisted of three cycles performed at a C-rate of 0.033.

For the accelerated calendar-aging test, the cells were first conditioned with the formation process. Following the formation, the cells were fully lithiated using a CCCV protocol (CC at 0.033 C, followed by CV at 0.01 V with a 0.01 C cut-off current) and subsequently stored at 45°C for 3 days. This storage-cycling sequence, which included three recovery cycles at 0.033 C between each storage period, was iteratively performed to quantify Li-inventory loss.

For the evaluation of cycling performance, the cells were tested after completing the same formation procedure. Subsequent long-term cycling was conducted via CCCV lithiation-delithiation protocol (CC at 0.2 C, followed by CV at 0.01 V for lithiation, and 1.5 V for delithiation, with a 0.02 C cut-off current) to maintain the stability of the electrochemical measurements throughout the evaluation.

Electrodes from disassembled cells were washed using dimethyl carbonate (DMC) inside the glove box to remove the residual electrolyte.

Reaction dynamics analysis (RDA) cell and analysis system: To investigate the reaction dynamics of the composite electrodes, a specialized RDA cell was designed, as illustrated in Fig. 2a. The overall assembly procedure followed that of a standard three-electrode coin-cell.⁴⁶ Lithium metal (450 μm thickness, 16 mm diameter) served simultaneously as both the reference and counter electrodes, while a thin copper wire acted as the lead connection. To avoid short-circuiting, the copper wire was insulated with Kapton tape and positioned between the positive case and the gasket so that it extended through the small gap between the upper and lower cases. Additionally, the space around the lead wire was subsequently sealed with epoxy resin to prevent air leakage.

Inside the RDA cell, the Li-metal electrode was arranged in a sandwich configuration between two working electrodes, with separators placed between each working electrode and the Li metal. The two working electrodes were externally short-circuited using a KEITHLEY DMM 6500 digital multimeter, effectively mimicking the particle-to-particle contact between Si and graphite in the composite electrode. The cell voltage and total applied current were recorded using a SINOPRO MRX CT-4008T battery tester, whereas the current flowing through the Si electrode was independently monitored via the KEITHLEY multimeter, as depicted in Fig. 2a.

The electrodes used in the Si10_R_cell were prepared with the same composition and properties as those in the standard coin-cell configuration. The mass ratio of graphite to Si was maintained at 89.95 wt. %:10.05 wt. % (corresponding to 1.216 mg of graphite and 0.136 mg of Si as active materials). To reproduce the practical environment of Si particles in composite anodes, the Si electrode for the RDA cell was formulated with 70 wt. % conductive carbon, reflecting the carbon-rich surroundings of Si typically composed of Super P and graphite. This design allows the RDA cell to realistically emulate the conductive network within Si-graphite composite electrodes and ensures reliable quantification of current distribution between the two components.

To quantitatively evaluate the reaction kinetics of each component, the currents flowing through the Si and graphite working electrodes (I_{Si} and I_{Graphite}) were normalized by the theoretical capacities of the respective electrodes (mAh). The resulting values were defined as the effective C-rates (h^{-1}), representing the actual current densities applied to the active materials of each electrode. This normalization allows direct comparison of the electrochemical responses of Si and graphite within the RDA cell, independent of their differences in capacity or mass loading.

X-ray photoelectron spectroscopy (XPS): XPS measurements for Fig. 1 and Fig. 3c–e were conducted using a PHI 5000 VersaProbe II system (Physical Electronics), while those for Fig. 6c–e and Fig. S11c–e were acquired using a NEXSA-G2 system (Thermo Fisher Scientific). Sample exposure to air was completely avoided because the XPS chamber was directly connected to an argon-filled glovebox. All spectra were calibrated to the C–C/C–H peak at 284.8 eV. Shirley background was subtracted from all

spectra. Peak fitting was carried out with CasaXPS®, and the resulting fitted data were exported and visualized using Origin®. Relative atomic concentrations were obtained from the integrated areas of Gaussian-fitted peaks.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS): ToF-SIMS measurements were carried out using an M6 instrument (IONTOF GmbH). To minimize air exposure, the samples were mounted onto a sample holder inside an argon-filled glove box and sealed within a vinyl pack filled with argon gas. The sealed pack was opened in a controlled laboratory environment with relative humidity maintained below 15%. Each specimen was introduced into the load-lock chamber within 15 s after unsealing, and the chamber pressure was reduced to below 1×10^{-6} mbar within 5 min. Depth profiling was performed under negative polarity mode through alternating analysis and sputtering cycles. A Bi_3^{2+} ion beam (30 keV, 0.2 pA) was used for analysis, and Cs^+ ions (1 keV, 90 nA) served as the sputtering source. The analysis and sputtering areas were set to $100 \mu\text{m} \times 100 \mu\text{m}$ and $300 \mu\text{m} \times 300 \mu\text{m}$, respectively. The normalized intensity was obtained by dividing the intensity of each detected species by the total intensity of all observed species.

Scanning spreading resistance microscopy (SSRM): Spreading resistance mapping was performed using an NX-10 system (Park Systems) operated in contact mode. To prevent degradation of the SEI layer, all measurements were conducted inside an Ar-filled glove box ($\text{H}_2\text{O}/\text{O}_2 < 0.1$ ppm). A conductive CDT-NCHR cantilever was used, and a bias voltage of 1.00 V was applied between the tip and the substrate. The scans were carried out at a frequency of 0.01 Hz. The three-dimensional spreading-resistance maps shown in Fig. 5a and Fig. 7a were reconstructed using the surface height and resistance data simultaneously acquired from the SSRM measurements.

Computational Details: Density Functional Theory (DFT) calculations were performed using the Vienna ab-initio simulation package (VASP) to understand SEI formation dynamics in silicon-graphite composite electrodes.⁴⁷ The exchange-correlation effect was described by the Perdew–Burke–Ernzerhof (PBE) within generalized gradient approximation (GGA).⁴⁸ The core and the valence electrons were treated by the projected-augmented wave (PAW) potentials and the plane-wave basis set with a cutoff energy of 520 eV.^{49,50} The DFT-D3 method with Becke-Johnson damping function was used to account for van der Waals interactions.⁵¹ All calculations were converged to electronic convergence criterion of 10^{-4} eV and atomic force tolerance of $0.05 \text{ eV}\text{\AA}^{-1}$. Spin-polarization was included for all systems.

To model silicon-graphite composite surfaces, the representative slab models for both materials were constructed, incorporating the most stable and commonly occurring surfaces as reported in the Materials Project and literature. ($\text{Si}(1\ 0\ 0)$ and $\text{Si}(1\ 1\ 1)$ facets for silicon, zigzag and armchair edges for graphite).^{52,53} The $\text{Si}(1\ 0\ 0)$ and $\text{Si}(1\ 1\ 1)$ slab models were built with eight layers, with nine Si atoms per layer. The simulation cell lengths were set to 11.55 Å in both the x and y direction. For graphite, zigzag- and armchair-edged structures were prepared with 11 and 12 layers, respectively, each layer comprising 16 C atoms. The periodic cell lengths were 9.87 Å along x and 15.61 Å along y direction for the zigzag model, and 8.55 Å along x and 15.61 Å along y for the armchair model. In all slab calculations, a vacuum

region exceeding 20 Å was introduced along z direction to avoid inter-slab interactions. Only the top three atomic layers were allowed to relax, while the remaining layers were fixed at their bulk-truncated positions. Brillouin-zone sampling was performed using Γ -centered k-point meshes of 4×4×1 for the Si(1 0 0) and Si(1 1 1) slabs, 5×3×1 for the zigzag graphite model, and 6×3×1 for the armchair graphite model.

The adsorption energy of additive on the surface is calculated as

$$\Delta E_{\text{ads}} = \Delta E_{\text{surf+addi}^*} - \Delta E_{\text{surf}} - \Delta E_{\text{addi}}$$

Where $E_{\text{surf+add}^*}$ and E_{surf} are the total energies of the surface with and without the additive, respectively. E_{addi} is the energy of the isolated molecule in vacuum. In addition, a Bader charge analysis was carried out to quantify charge transfer and assess the reduction behavior of the adsorbed additive.⁵⁴

Declarations

Conflicts of interest

There are no conflicts to declare.

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Figures

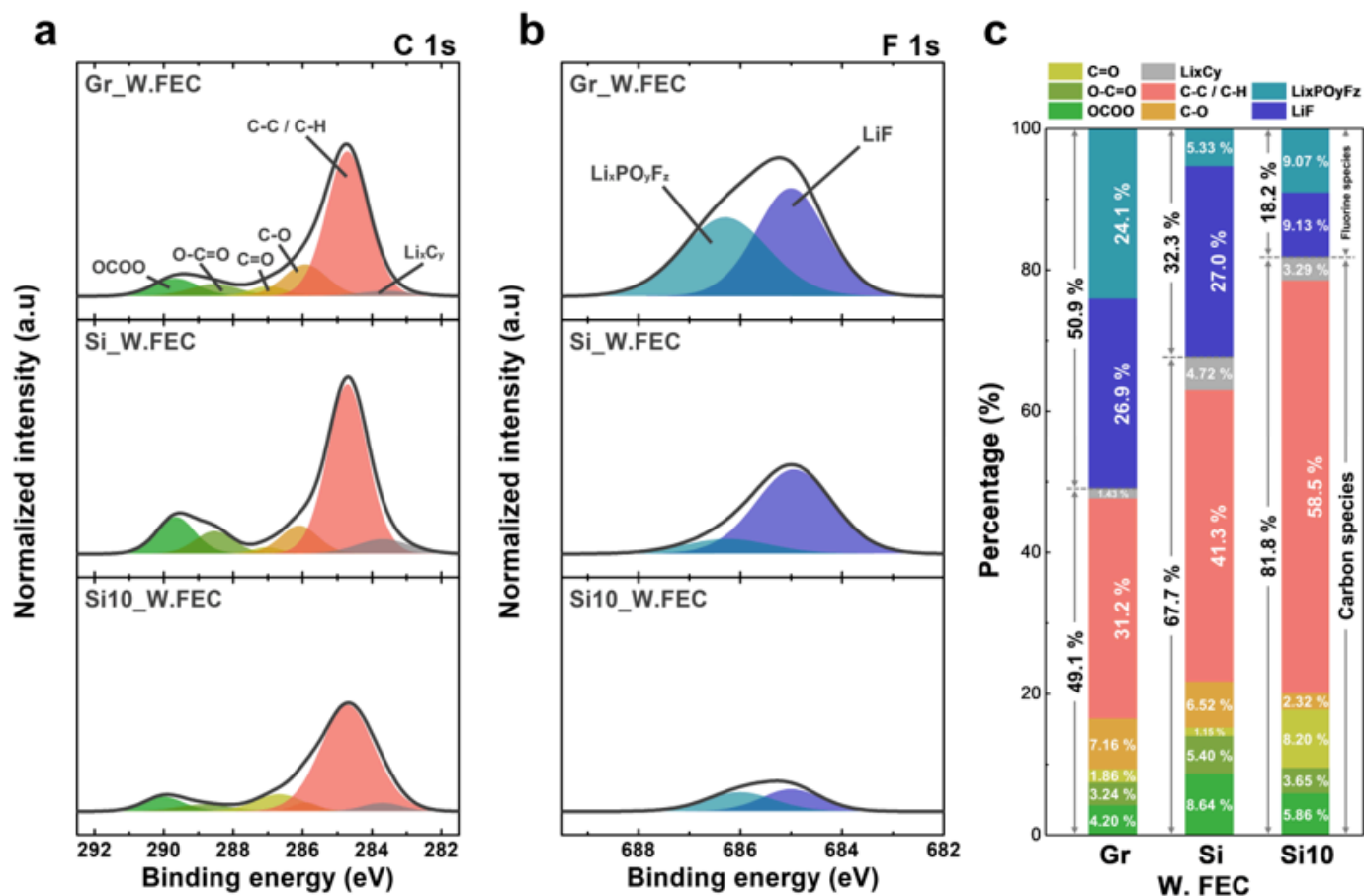


Figure 1

Material-dependent SEI composition revealed by XPS after the first lithiation. (a) C 1s and (b) F 1s spectra of Gr_W.FEC, Si_W.FEC, and Si10_W.FEC electrodes. (c) Quantitative distribution of carbon- and fluorine-related surface species; the stacked bars represent the relative contributions of C 1s (bottom) and F 1s (top) components, with bracketed values denoting the overall carbon and fluorine fractions (the latter defined as the F-ratio). Numerical data are provided in Table S1.

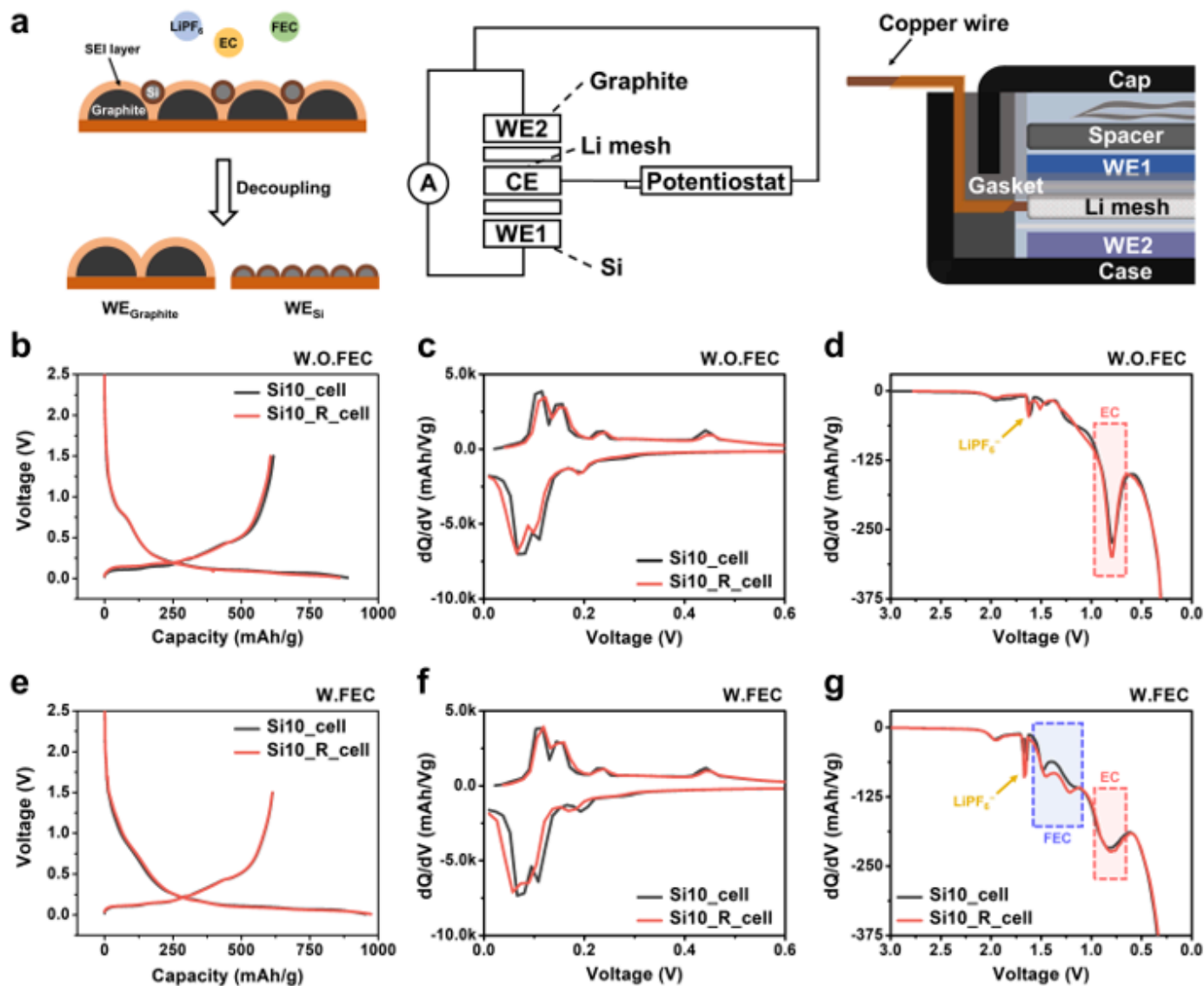


Figure 2

RDA cell design and validation against conventional coin-cells. (a) Schematic of the RDA cell and measurement system. (b, e) Capacity vs. voltage and (c, f) dQ/dV vs. voltage curves during the initial cycle at 0.033 C for both the Si10_cell (black) and Si10_R_cell (red): (b–d) W.O.FEC; (e–g) W.FEC. (d, g) Enlarged views of the 0.5–3 V region from (c) and (f), respectively. Shaded regions indicate reductive decomposition ranges of EC (red) and FEC (blue); the orange arrow marks LiPF₆ reduction.

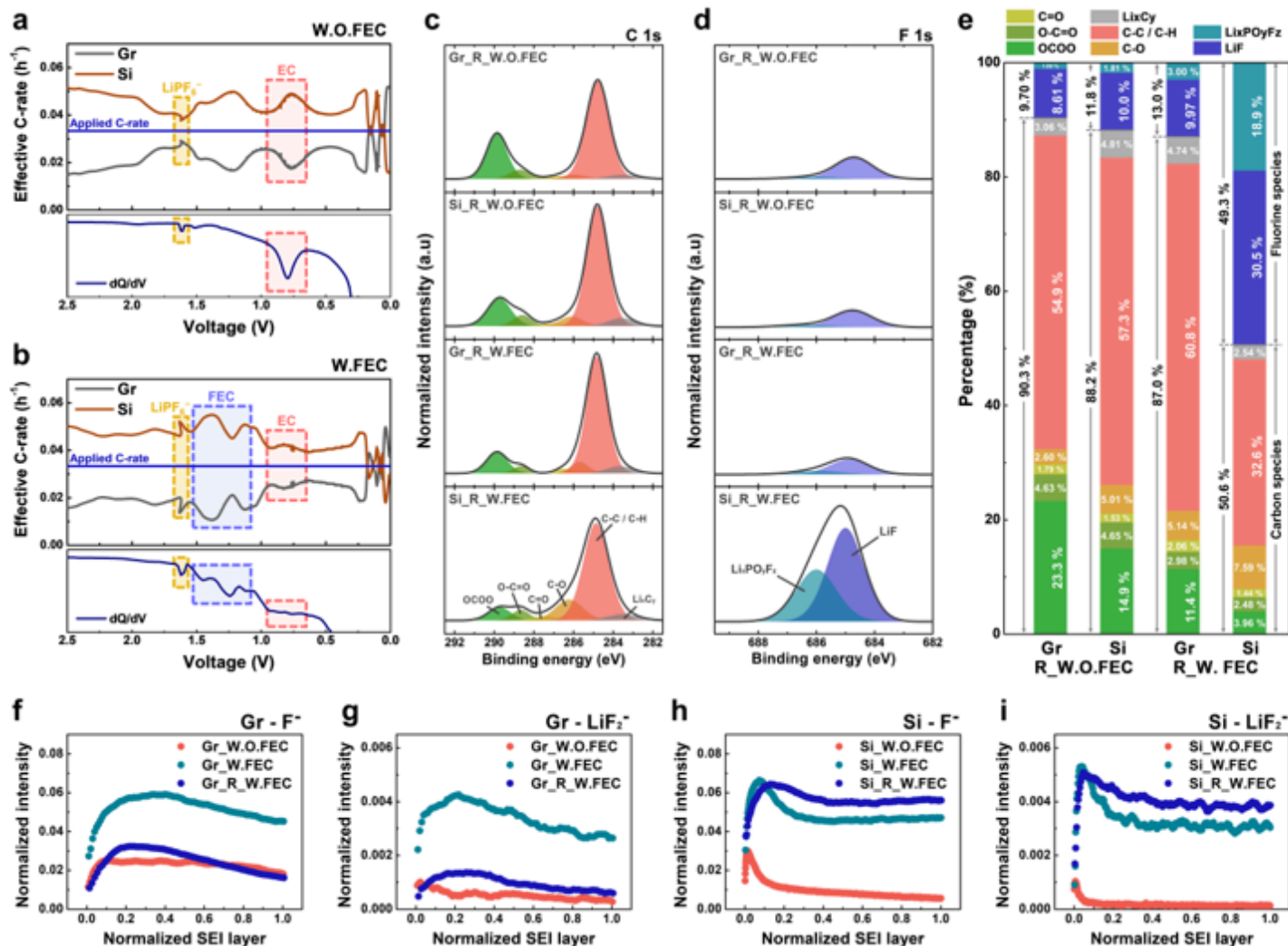


Figure 3

Phase-resolved SEI formation dynamics and interfacial chemistry in Si10_R cells. (a–b) Effective C-rate vs. voltage profiles (top) and dQ/dV curves (bottom) during the first lithiation: (a) W.O.FEC and (b) W.FEC. The blue line indicates the applied C-rate. (c–e) XPS analysis of electrodes harvested from Si10_R cells: (c) C 1s and (d) F 1s spectra; (e) quantitative distribution of carbon- and fluorine-related surface species, with bracketed values denoting the overall carbon and fluorine fractions (the latter corresponding to the F-ratio); numerical data in Table S3. (f–i) ToF-SIMS depth profiles of F⁻ and LiF₂⁻ ions for harvested graphite (f–g) and Si (h–i) electrodes. Intensities are normalized to the total ion count; the SEI/bulk boundary (normalized depth = 1.0) is defined in Fig. S5.

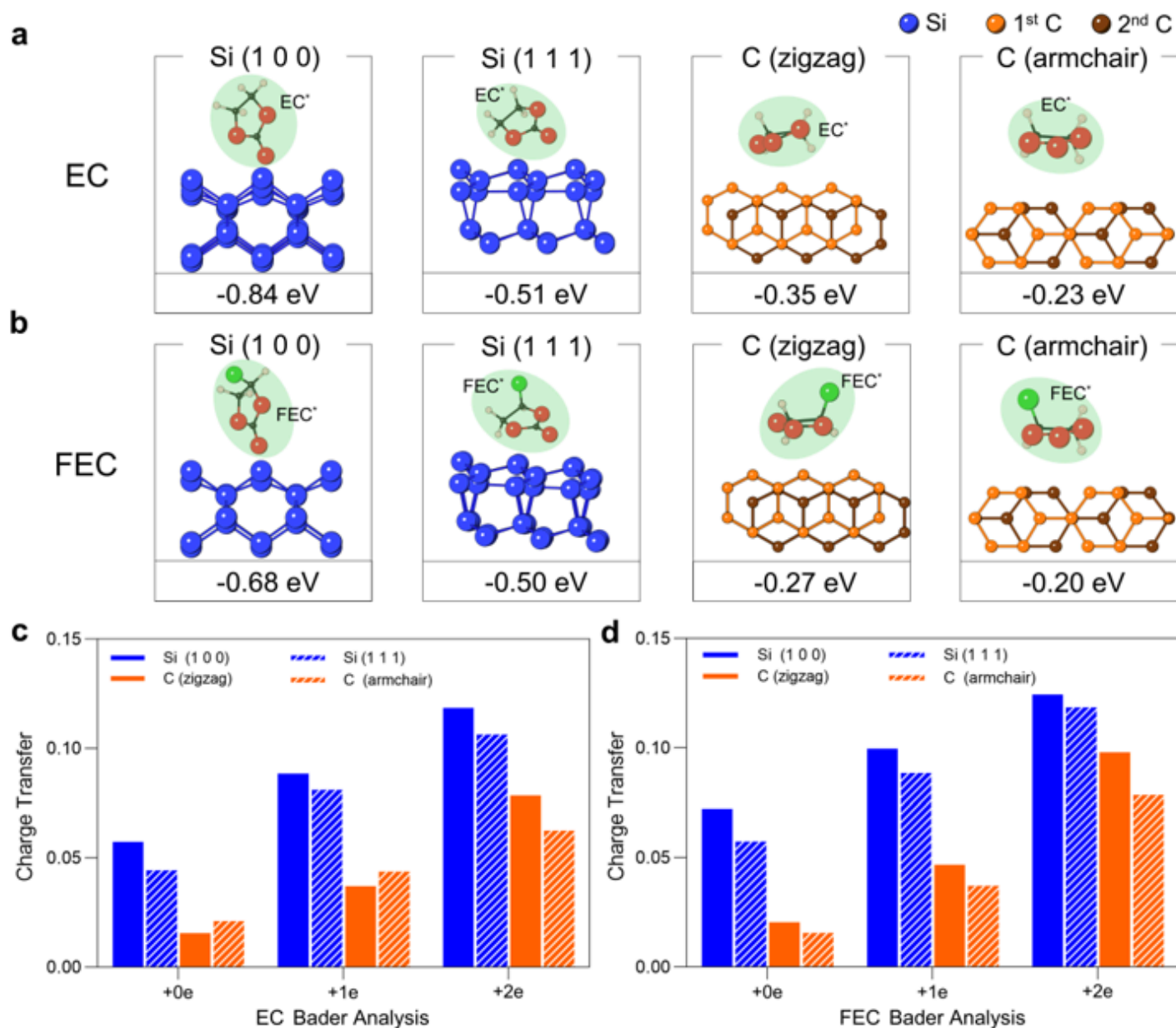


Figure 4

DFT based calculations of EC and FEC decomposition reactions during SEI formation. Calculated adsorption energies of electrolyte components on Si (100), Si (111), C (zigzag), and C (armchair) surfaces: a) EC, b) FEC. Bader analysis of charge transfer between electrolyte components and anode surfaces, compiled based on electron number: c) EC, d) FEC.

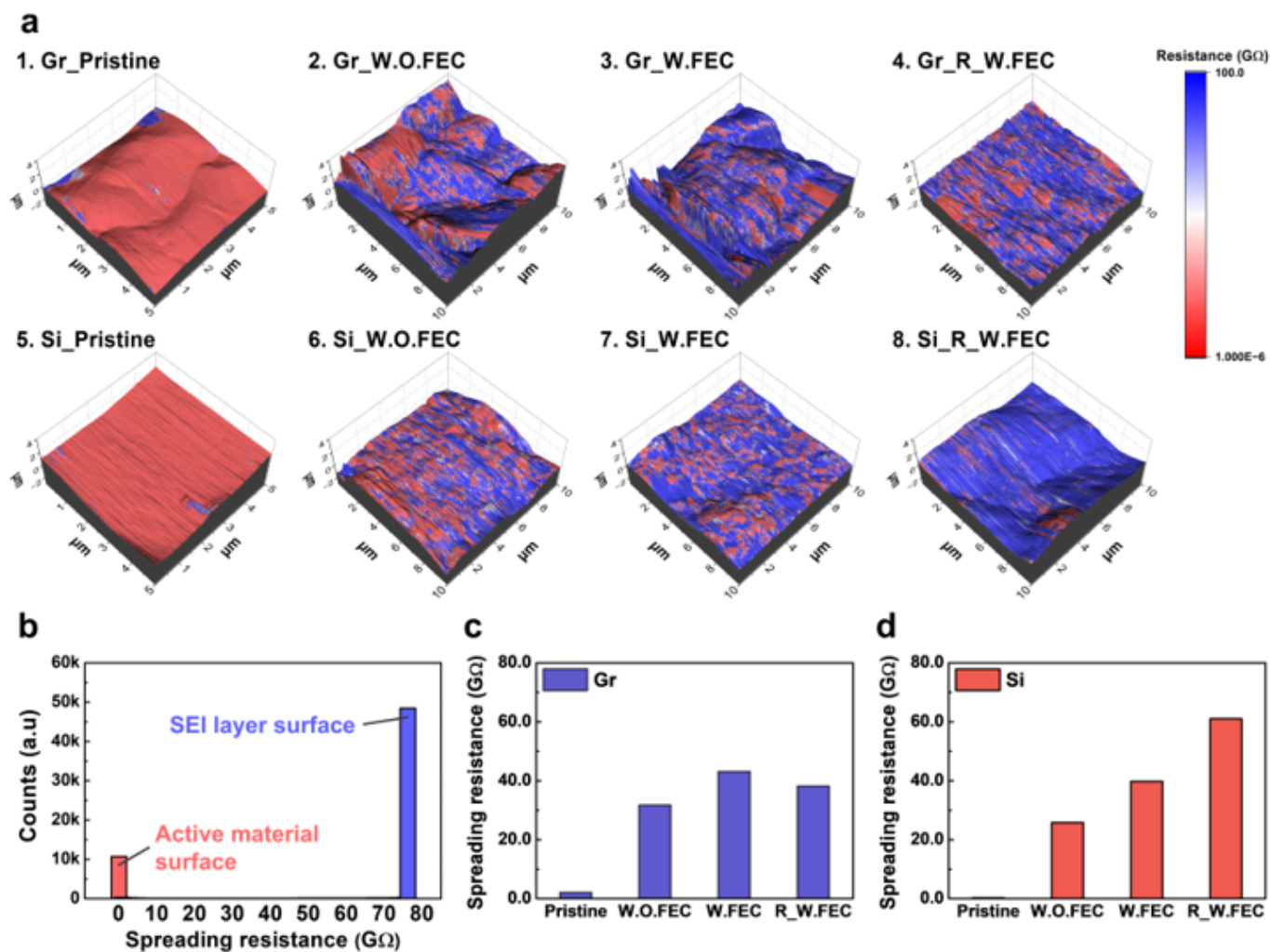


Figure 5

Asymmetric FEC decomposition produces disparate SEI passivation on Si and graphite. (a) Three-dimensional spreading-resistance maps of pristine and harvested electrodes: (1) Gr_Pristine, (2) Gr_W.O.FEC, (3) Gr_W.FEC, (4) Gr_R_W.FEC, (5) Si_Pristine, (6) Si_W.O.FEC, (7) Si_W.FEC, (8) Si_R_W.FEC. (b) Representative resistance histogram for Si_R_W.FEC (panel a-8), illustrating the bimodal distribution corresponding to the SEI layer and the active-material surface. Average spreading resistance for (c) graphite and (d) Si electrodes extracted from the maps in (a)

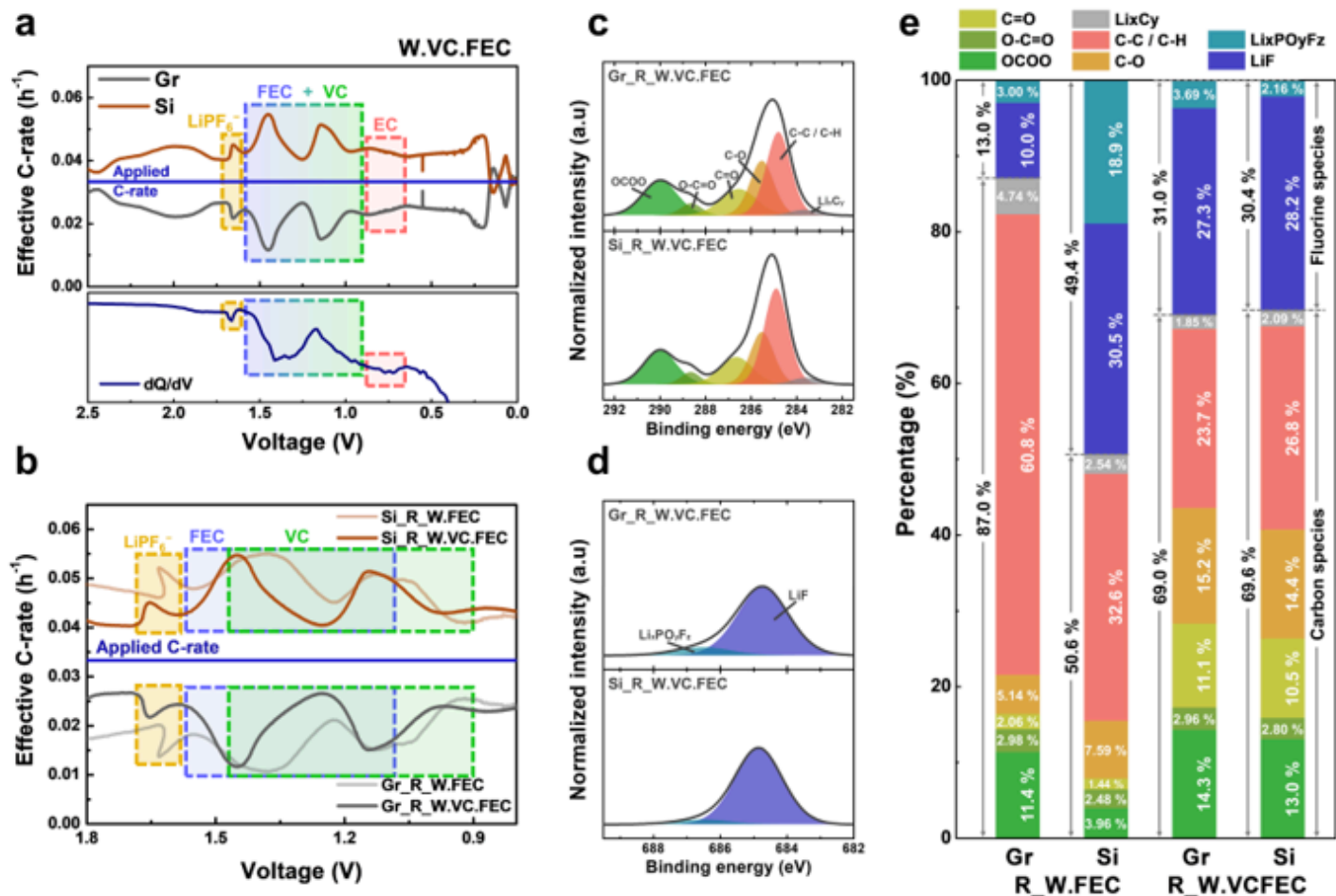


Figure 6

Co-additive strategy redistributes electrolyte decomposition and produces compositionally uniform SEI on both phases. (a) Effective C-rate vs. voltage profiles (top) and dQ/dV curves (bottom) of the Si10_R_cell under W.VC.FEC condition during the first lithiation. (b) Overlaid comparison of the decomposition region (0.8–1.8 V) for W.FEC (from Fig. 3b) and W.VC.FEC conditions, showing the narrowing of the Si current hump and concurrent rise in graphite current under the co-additive condition. (c) C 1s and (d) F 1s spectra of Gr_R_W.VC.FEC and Si_R_W.VC.FEC. (e) Quantitative distribution of carbon- and fluorine-related surface species; the stacked bars represent the relative contributions of C 1s (bottom) and F 1s (top) components, with bracketed values denoting the overall carbon and fluorine fractions (the latter defined as the F-ratio). W.FEC data (Gr_R_W.FEC and Si_R_W.FEC) are re-plotted from Fig. 3e for comparison; numerical data in Table S4.

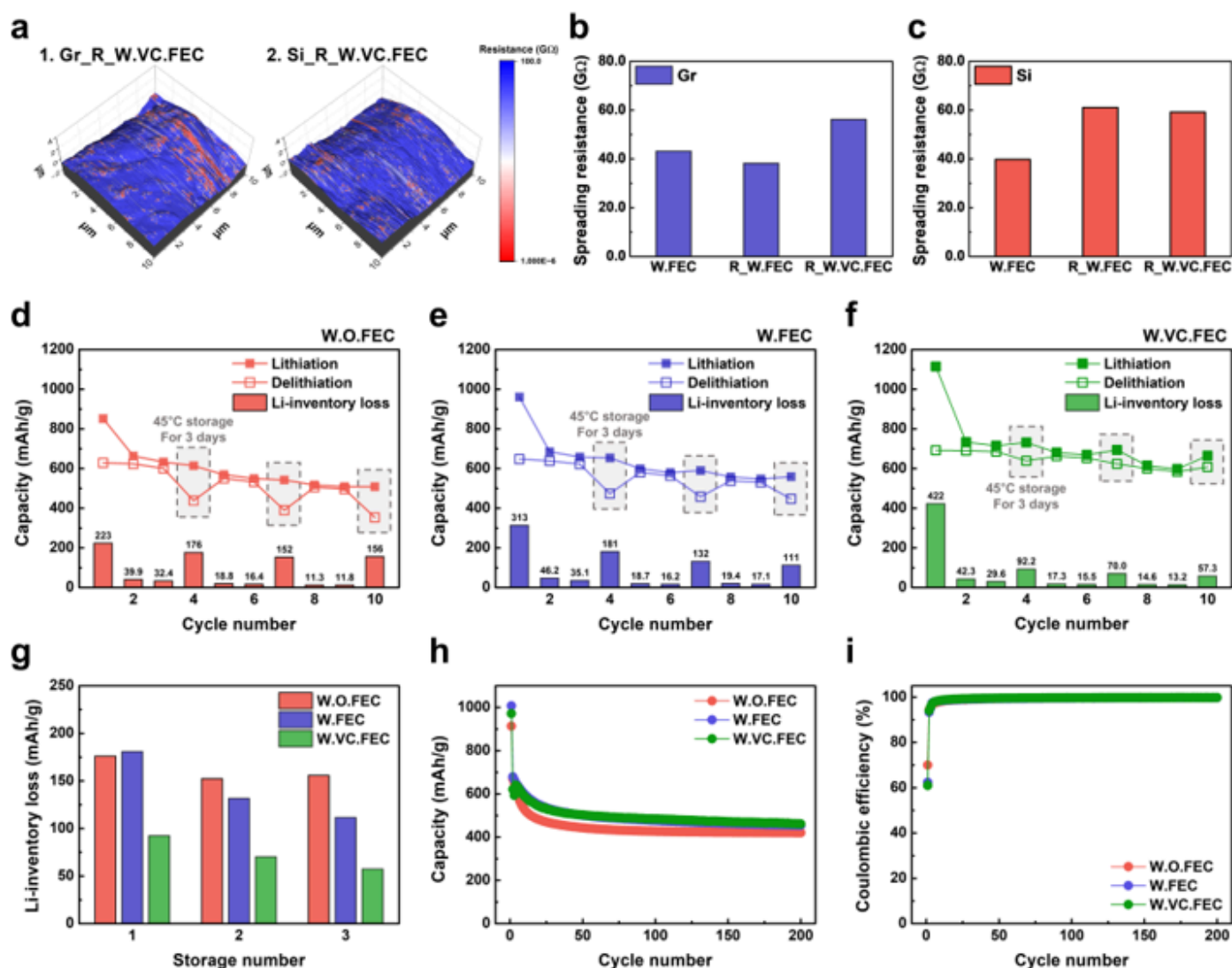


Figure 7

Quantitative comparisons of SEI stability under different electrolyte conditions. SSRM analysis of harvested electrodes after the first lithiation: (a) Three-dimensional spreading-resistance maps of Gr_R_W.VC.FEC and Si_R_W.VC.FEC electrodes. (b–c) Comparison of average spreading resistance values extracted from SSRM data: (b) Gr_W.FEC and Gr_R_W.FEC values are re-plotted from Fig. 5c for comparison; Gr_R_W.VC.FEC is from the map in (a-1). (c) Si_W.FEC and Si_R_W.FEC values are re-plotted from Fig. 5d; Si_R_W.VC.FEC is from the map in (a-2). Capacity retention and Li-inventory loss during accelerated calendar-aging at 45 °C after full lithiation by the CCCV protocol (CC at 0.033 C, followed by CV at 0.01 V with a 0.01 C cut-off current) for cells with (d) W.O.FEC, (e) W.FEC, and (f) W.VC.FEC conditions following high-temperature storage. (g) Comparison of the Li-inventory loss shown in Fig. 7d–f. (h) Specific capacity and (i) coulombic efficiency vs. cycle number of Si10_cells with W.O.FEC, W.FEC, W.VC.FEC conditions under 0.2 C-rate.

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