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Revisiting potassium intercalation in graphite: an *operando* characterisation and computational approach

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Potassium-ion batteries (KIBs) with graphite anodes are emerging as a highly promising “beyond lithium” technology driven by battery demands, potassium’s abundant reserves and the inherent similarities in intercalation chemistry to lithium-ion systems. Despite this potential, a understanding of potassium intercalation into graphite, particularly concerning early intercalation stages and the in-plane ordering of K⁺ within graphite intercalation compounds (GICs), lacks sufficient elucidation. Herein, we employed a multi-modal, *operando* characterisation approach to elucidate the correlation of electrochemical potassiation and structural evolution in graphite, hence unravelling the specific mechanisms of K-ion storage. *Operando* electrochemical dilatometry precisely quantifies the macroscopic volume expansion of a graphite electrode during potassiation. Meanwhile, *operando* synchrotron X-ray diffraction (XRD) records ordered phase transitions during early-stage intercalation, detailing the formation of distinct GIC phases. Furthermore, Raman spectroscopy and density-functional theory (DFT) reveal the in-plane ordering of K⁺ within the graphite gallery and stacking modes. *Operando* optical microscope and UV-vis spectroscopy together provide insights into the changing optical properties, linking these changes to different GICs and electronic structural changes. This comprehensive study offers fundamental mechanistic insights into K-ion storage in graphite, paving the way for the rational design of high-performance KIB anodes.

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Broader context

The global push for sustainable energy solutions and grid-scale storage has underscored the limitations of lithium-ion batteries (LIBs), particularly concerning the cost and geopolitical constraints of related resources. This situation has driven intense research into “beyond lithium” technologies that use more abundant elements. Among these, sodium-ion batteries and potassium-ion batteries (KIBs) have emerged as highly promising and scalable alternatives. KIBs feature a similar intercalation chemistry to LIBs while benefiting from the vast and widely distributed reserves of potassium. A key challenge in the commercialisation of KIBs lies in the development of high-performance and long-lasting electrode materials. Carbonaceous materials, especially graphite, are the main candidates for KIB anodes due to their high gravimetric capacity and industrial maturity. However, the larger ionic radius of potassium leads to different intercalation dynamics compared to lithium, and a comprehensive, in-depth understanding of the real-time structural and electronic changes that occur during potassiation is critically needed to inform the rational design of next-generation KIBs. This work addresses this fundamental knowledge gap by investigating the intercalation mechanisms of potassium in graphite.

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In 2024, a startup GROUP1 launched the world's first K-ion 18 650 cylindrical batteries with graphite anode and a cell energy density of 160–180 Wh kg⁻¹, benchmarking the current

The electrochemical performance of graphite as an anode material for KIBs was characterised in a three-electrode configuration: K metal|1 M KN(SO₂F)₂ (KFSI) in ethylene carbonate (EC) and diethyl carbonate (DEC) (1 : 1 in volume) |graphite

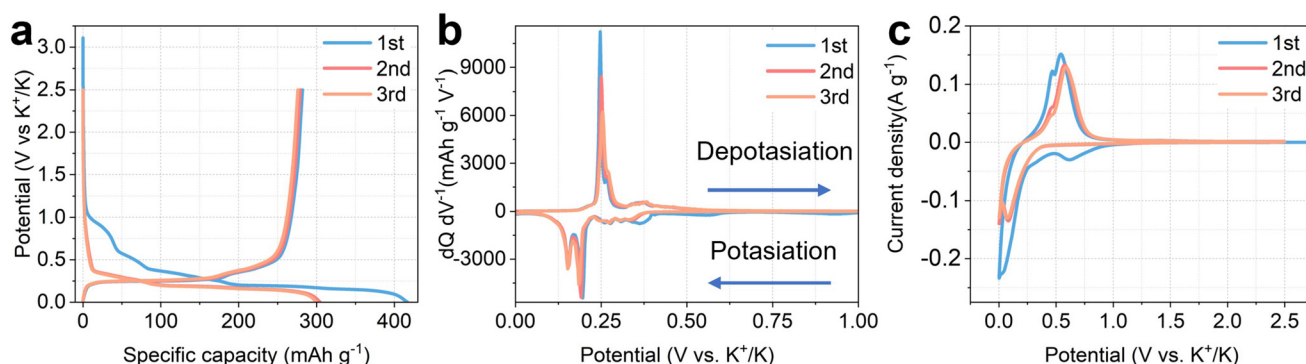


Fig. 1 The electrochemistry of K metal|1 M KN(SO₂F)₂ in EC and DEC (1 : 1 in volume)|graphite batteries. (a) The first three galvanostatic discharge–charge cycles at 16 mA g⁻¹; (b) the differential capacity of the first three galvanostatic discharge–charge cycles; (c) the first three cyclic voltammetry (CV) profiles at 0.1 mV s⁻¹.

(Fig. 1a). Fig. S1 shows the characterisation of the graphite. This electrolyte composition was chosen due to several compelling advantages over alternatives. The 1 M KFSI in EC/DEC electrolyte offers stable electrochemical performance during cycling (Fig. S2 in SI), consistent with reported literature.^{10,14,15} Additionally, it was reported that this electrolyte system demonstrates a high initial coulombic efficiency (up to 89%) and higher ionic conductivity (10.7 mS cm⁻¹).²⁸ In contrast, the widely adopted slat KPF₆-based electrolytes show lower initial coulombic efficiencies (50–60%) and limited solubility of up to 0.8 M in EC : DEC.²⁹ A critical consideration for long-term cell stability is the interaction with current collectors. It is worth noting that the use of a pure KFSI electrolyte, free from chloride impurities, is expected to mitigate corrosion of the Al current collector commonly employed on both the anode and cathode sides, thereby ensuring the overall cell lifespan.^{28,30}

All discharge (potassiation) and charge (depotassiation) profiles exhibit a sloping region at high potential and a long plateau capacity at low potential. The observed plateau regions are reflected as sharp peaks in the differential capacity plot shown in Fig. 1b. The electrochemical potentials associated with K⁺ intercalation into graphite determine the overall cell voltage and therefore energy density. This differential capacity plot indicates that K⁺ intercalation into graphite occurs at *ca.* 0.1–0.2 V vs. K^{+/K}. This value is slightly higher than those observed for the Li case (*ca.* 0.1 V vs. Li^{+/Li}), which suggests a lower likelihood of K metal plating. Cyclic voltammetry (CV) was conducted at a scan rate of 0.1 mV s⁻¹ (Fig. 1c) for the first three cycles. The first cycle features an increased CV area attributed to solid electrolyte interphase (SEI) formation, in line with a higher discharge (potassiation) capacity. It is widely accepted that the formation of an SEI is the main reason for the irreversible loss in KIBs, which will be discussed in section 2.5.

Regarding the notation, the stage index *n* is extensively employed to describe the periodic stacking of K-GIC. The stage index, denoted as *n* (an integer: 1, 2, 3, *etc.*), describes the number of graphite layers between two adjacent intercalated

potassium layers. Diffraction patterns play a crucial role in identifying these staged structures. The stage diffraction [00*n*] peak serves as a definitive indicator of staging behaviour in K-GICs, indicating the periodic repetition of intercalant layers along the crystallographic *c*-axis. It is important to clarify the [00*n*] notation: while Miller indices (*hkl*) incorporate the in-plane ordering of the potassium layers, it instead functions as a classification system specifically tailored for describing the characteristic layering patterns observed in GICs. In contrast to the macroscopic *c*-axis staging described by the stage index and [00*n*] stage diffraction, Miller indices (*hkl*) are utilised to consider the in-plane ordering of the potassium layers. This distinction is crucial for a complete structural description. For example, in stage 1 KC₈, the Miller index (00*l*) quadruples relative to the stage diffraction [001] due to a difference in-plane ordering is considered.

Furthermore, the in-plane potassium ordering is denoted using the notation *p*(*A* × *B*)*R**φ*, where *p* stands for primitive, *A* and *B* are the in-plane lattice parameters, and *φ* defines the rotational angle between the intercalated lattice and the graphite cell vectors. For example, *p*(2 × 2)*R*0° means this unit cell is twice as long as the graphite unit cell along both of its principal axes in the plane, and the potassium superlattice is perfectly aligned (no rotation) with the underlying graphite lattice. This detailed notation allows for a precise characterisation of the potassiation of graphite.

2.2. Electrode-level changes via *operando* dilatometry

Understanding the dynamic volume changes of electrode materials during cycling is crucial for designing long-lasting KIBs. *Operando* electrochemical dilatometry, as shown in Fig. 2a, provides the periodic thickness variations of a graphite electrode in the first five discharge–charge cycles at 16 mA g⁻¹. The pristine graphite electrode measures 61.1 μm in thickness (after calendaring). During the first potassiation cycle, the graphite electrode experienced a significant dilation of 29.7 μm (from 61.1 μm to 90.8 μm), which accounted for 48.6% of the thickness of the pristine graphite, representing the most pronounced expansion observed across all five cycles.



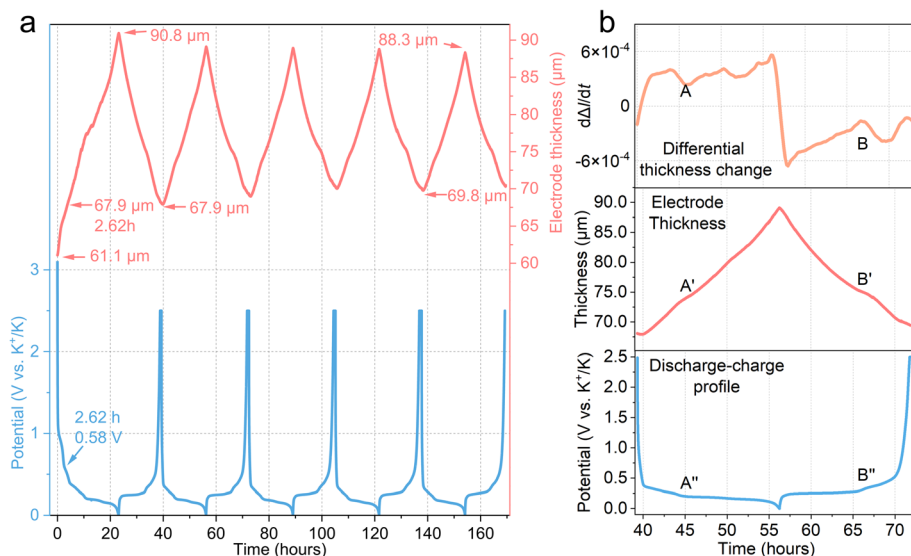


Fig. 2 *Operando* electrochemical dilatometry analysis. (a) For the first five cycles (in blue) at 16 mA g^{−1}, with the change in thickness (in pink). The thickness of the pristine graphite electrode is 61.1 μm; (b) the change of the electrode thickness and its differential change in the second cycle.

This initial expansion is a critical behaviour of the first potassiation process. Following the first de-potassiation cycle, the electrode partially contracts to 67.9 μm, which is still equivalent to 110.3% of the pristine graphite thickness. The initial expansion of 6.8 μm, between OCV (61.1 μm) and 0.58 V (67.9 μm) in the first cycle, is primarily attributed to the formation of the solid electrolyte interphase (SEI) layer and irreversible potassiation,³¹ which is in line with the CV analysis above. Apart from the SEI formation, the irreversible expansion after the first cycle is mainly attributed to irreversible potassiation,^{6,32} which is discussed in the *operando* microscope analysis (in section 2.4). For context, the theoretical *c*-axis expansion from pristine graphite (3.35 Å) to fully potassiated graphite KC₈ (5.35 Å) is 60%. In comparison, a Li||graphite cell exhibits a much smaller initial thickness dilation. It is reported that a full lithiation causes only *ca.* 8.8% thickness dilation, including an irreversible thickness change of *ca.* 3.5%, while the theoretical *c*-axis expansion is *ca.* 10.4% from 3.35 Å (graphite) to *ca.* 3.70 Å (stage 1 Li-GICs, LiC₆).³³ This comparison highlights the significantly larger volume changes by K⁺ intercalation compared to lithium.

Following each depotassiation, a constant voltage of 2.5 V was applied until the current decreased to 1.6 mA g^{−1} to remove as much K⁺ as possible before a new potassiation cycle. In the first five cycles, a clear trend emerges that the thickness of the graphite electrode at the fully potassiated state gradually decreases, while, conversely, it gradually increases at the fully depotassiated state. In the fifth cycle, the full potassiation only causes an expansion of 18.5 μm from 69.8 μm to 88.3 μm. This suggests that the graphite parties rearrange to maintain a stable structure over cycles.

Fig. 2b provides a detailed investigation of the thickness change during the 2nd cycle, alongside its time derivative (dΔL/dt), which directly represents the rate of thickness

change. Analysing dΔL/dt reveals two key points where the absolute value of the rate of thickness change reaches a minimum, indicating the slowest rates of dimensional variation. These minima occur around the 46th hour (point A) and the 67th hour (point B). Based on the corresponding electrochemical profiles, these minimal changes occur after the formation of stage 3 KC₂₄. We hypothesise that a “liquid-like” stage 2L occurs, leading to the small plateau in the thickness rate between stage 3 KC₂₄ and stage 2 KC₁₆. From the literature, *operando* pressure measurements and electrochemical dilatometry reveal that Li||graphite cells exhibit a small pressure and thickness change during the transition between stage 3 and stage 2.^{31,34} This feature of minimal changes observed in our K||graphite system suggests that the stage 2L observed in Li-GICs also occurs in potassium intercalation.

A more rapid and notably linear correlation between thickness change and capacity is observed at the end of potassiation and the beginning of depotassiation (formation of stage 1 K-GIC), around the 56th hour in Fig. 2b. This fastest change in electrode thickness is primarily attributed to the dilation/contraction of the *c*-axis of graphite during the phase transition between stage 2 (average *d*-spacing = 4.35 Å) and stage 1 (average *d*-spacing = 5.35 Å). This stage transition involves a larger change in the average *d*-spacing than any other stage transitions in K-GICs. The observed linear change can be further elucidated by considering an “accordion-like” mechanism of intercalation, where not all K⁺ intercalate into each empty graphene interlayer but instead progressively move the graphite layers apart.³⁵

2.3. Atomic expansion *via* synchrotron X-ray diffraction

To gain atomic-level insights into the expansion behaviour of the graphite anode during electrochemical potassiation, we conducted *operando* synchrotron X-ray diffraction (XRD) at



Diamond beamline I15-1. For these measurements, we used a Diamond Radial *In situ* X-ray (DRIX) cell.³⁶ The DRIX cell is custom-designed for *in situ* and *operando* experiments. In this experiment, the pristine graphite is potassiated under an extremely low current of 6.5 mA g⁻¹ to ensure the early stages are captured. The potassiation process was stopped until the stage 1 K-GIC is partially formed, evident by the co-existence of characteristic diffraction peaks for both stage 1 KC₈ and stage 2 KC₁₆.

At the very early stages of potassiation, when K⁺ concentrations are low, K⁺ intercalation into graphite is known to be energetically unfavourable.^{37,38} However, with potassiation proceeds, the initial intercalation events induce a crystallographic expansion along the *c*-axis. This expansion can lower the energy barrier for subsequent intercalation.³⁹ Fig. 3a illustrates this process that the pristine graphite (002) peak initially observed at $Q = 1.878 \text{ \AA}^{-1}$ ($d_{\text{interlayer}} = 3.35 \text{ \AA}$) and then splits into two new peaks: (1) one located appears in high Q region (larger than $1.878 \text{ \AA}^{-1}$), which is associated with $[00(n+1)]$ stage diffraction of higher-stage K-GICs; (2) $[00n]$ stage diffraction appears in the lower Q region (smaller than $1.878 \text{ \AA}^{-1}$). Indeed, the intercalation of K⁺ opens the d -spacing of two graphene layers to *ca.* 5.35 Å, clearly confirmed by the appearance of the characteristic KC₈'s peak at $1.175 \text{ \AA}$, while the d -spacing of the empty graphene layers (those not yet intercalated) largely remains at 3.35 Å. This observation aligns well with established literature on K-GICs.^{6,7,14,15} Based on these struc-

tural observations, the *c*-axis periodicity of the K-GICs can be described mathematically. The total distance along the *c*-axis (d_c) of the minimal repeating unit in a stage n K-GIC can be calculated as follows:

$$d_c = d_{\text{K layer}} \times (n - 1) + d_{\text{graphite}}$$

where: $d_{\text{K layer}}$ is the expanded interlayer by potassium (5.35 Å); n is the stage number, d_{graphite} is the spacing of pristine graphite layers (3.35 Å).

The average d -spacing of the stage n is denoted as d_{00n} , which is calculated as follows:

$$d_{00n} = \frac{I_c}{n}.$$

And the relationship between the d_{00n} and d_{00n+1} is as follows:

$$\frac{d_{00n+1}}{d_{00n}} = \frac{n+1}{n}.$$

For example, the d_c , d_{001} , d_{002} and d_{003} of the stage 1 K-GIC is 5.35 Å, 5.35 Å, 2.68 Å and 1.78 Å, respectively. Similarly, the d_c , d_{001} , d_{002} and d_{003} of the stage 2 K-GIC is 8.70 Å, 8.70 Å, 4.35 Å and 2.90 Å, respectively.

DFT calculations suggest that significant local curvature in the graphene layers is induced during early intercalation.³⁸ Localised curvature can disrupt the long-range planar order of graphite, leading to a noticeable decrease in the intensity of

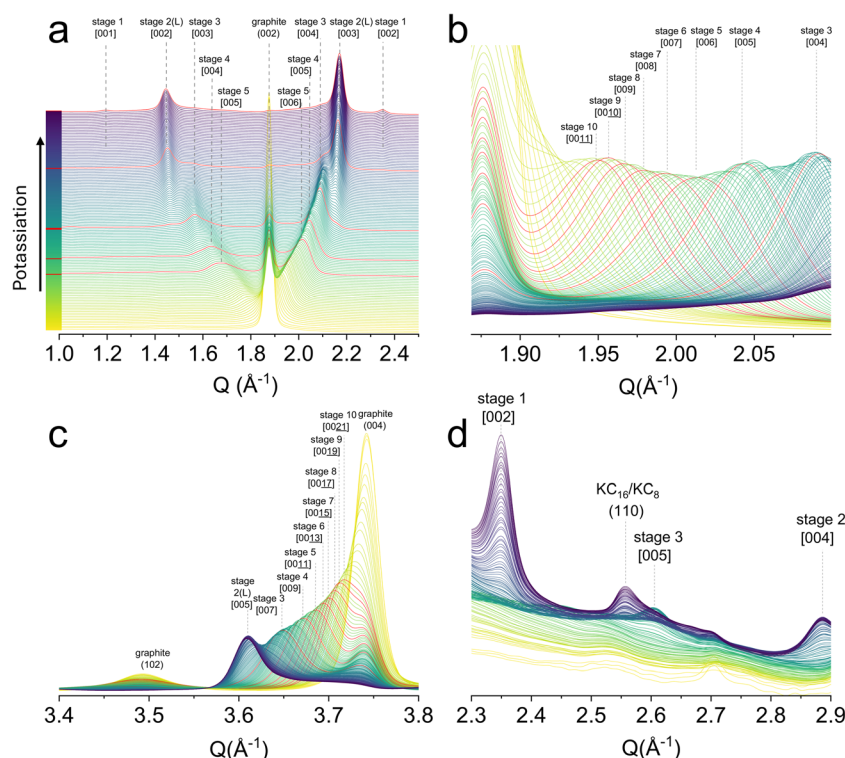


Fig. 3 Operando synchrotron X-ray diffraction patterns for the first potassiation cycle (a) Q range from 1.0–2.5 Å⁻¹, the highlighted red patterns are K-GICs stage 2–5 and stage 1/stage 2, stage 2L exists between stage 3 and stage 2; (b) Q range from 1.85 to 2.2 Å⁻¹; (c) Q range from 3.4 to 3.8 Å⁻¹; (d) Q range for the formation of [002] and [003] of stage 2 KC₁₆.



the pristine graphite (002) diffraction peak. Furthermore, compared with the rigid Rüdorff–Hofmann theory for ion intercalation,⁴⁰ the Daumas–Hérol domain model offers a more nuanced and widely accepted picture for K-GICs.¹⁵ This model suggests that K-GICs can consist of many microscopic, localised domains, even in the same stage, but with the intercalants in different domains occupying different interlayer galleries. Instead of maintaining long-range order, localised structural deformations occur, transitioning to short-range order, as further confirmed by *operando* XRD and *ex situ* transmission electron microscopy (TEM) images (in section 2.5). The structural instability is further exacerbated by the gradual leaching of K⁺ from the graphite lattice, which contributes to the observed weakening of the graphite (002) peak's intensity. According to the Scherrer equation, smaller coherent scattering domains lead to broader diffraction peaks, consistent with the observed characteristics. A detailed analysis of these structural transformations, including *c*-axis stacking and *ab*-plane ordering, will be discussed in section 2.5.

***c*-Axis stacking.** The staging behaviour of K-GICs during early intercalation remains a topic of considerable interest. Our synchrotron *operando* XRD reveals an ordered transition from graphite to high-stage K-GICs to low-stage K-GICs (see Fig. 3a). The *Q* range was selected from 1 to 2.5 Å⁻¹, where all the [00*n*] and [00(*n* + 1)] stage diffractions of stage *n* are concentrated. More importantly, a crucial observation from the data is that the [00(*n* + 1)] diffraction peak of a given stage *n* consistently exhibits higher intensity and is better resolved than its [00*n*] counterpart across all observed stages. This phenomenon agrees well with the theory by Leung *et al.*, which suggests the maximum peak intensity in GICs occurs at [00(*n* + *m*)] peak, where *m* is 0 and 1 for Li-GICs and K-GICs, respectively.⁴¹ These differences result from the size of different intercalated ions and the structure factor of X-rays. Consequently, we have chosen to focus on the well-resolved [00(*n* + 1)] peaks for studying the structural evolution of K-GICs, especially for high stages.

To our best knowledge, all previous literature using *operando* XRD shows a broader peak with a low intensity for high stages during early intercalation, regardless of whether [00*n*] or [00(*n* + 1)] peaks were studied. This limitation may stem from the long exposure times of lab-based XRD systems, which are not powerful in distinguishing the rapid, dynamic changes occurring in the early stages of intercalation. The inherent advantages of synchrotron XRD, including its high flux, low background noise, and short data acquisition times, are instrumental in effectively capturing the rapid evolution of these early-stage phases in our study. From the XRD pattern in Fig. 3b, the [00(*n* + 1)] peaks of K-GICs progressively shift to higher *Q* values as more K⁺ is intercalated. Within these K-GICs stages, the continuous shift of peaks towards a higher *Q* range means that a single-phase, ordered reaction is predominantly taking place. Notably, the [00(11)] corresponding to stage 10 appears as the first well-resolved phase. The regions between graphite and stage 10 present those stages that have not yet intercalated or are in very dilute stages, maintaining a graphite-like spacing.

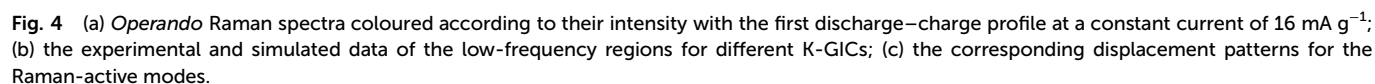
Peak fitting of the XRD patterns was conducted using the Voigt function from stage 10 to stage 5, and their intensity and full width at half maximum (FWHM) are summarised in Fig. S3 (SI). The FWHM of the [00(*n* + 1)] peaks remained consistent, ranging between 0.071 Å⁻¹ to 0.084 Å⁻¹ from stage 10 to stage 5, importantly, no sudden fluctuations in intensity and FWHM were observed. Instead, in the event that multiple high K-stages were coexisting prominently during the early stages, a massive increase in the FWHM of the peaks would be anticipated. The absence of such a broadening feature further supports a relatively smooth, ordered stage evolution. Additionally, the order transition from graphite's (004) peak to stage diffraction [00(2*n* + 1)] was also identified (Fig. 3c), complementing the evidence of the smooth phase change in the high stages. However, it must be noted that stage coexistence cannot be entirely avoided due to the relatively low K diffusivity within the solid graphite electrode,³⁸ particularly in thick samples (>120 μm) where voltage hysteresis is ubiquitous. Our findings, different from all previous literature, suggest a more ordered early-stage intercalation process compared to previously obtained results with lab-based XRD techniques.

Apart from the early stages, the existence of stage 2L, a proposed partially intercalated variant of stage 2, remains arguable in K-GICs. While Liu *et al.* proved a metastable stage 2L K-GICs using Raman spectroscopy.¹⁴ *Operando* microscope analysis (details in section 2.4) is in line with this phenomenon, which visualises the coexistence of phases (*e.g.*, stage 2 (orange) and stage 3 (blue), or stage 2 (orange) and stage 1 (gold)) during these two-phase reactions. In Li-ion cases, Fujimoto *et al.* proved the phases of stage 2 and stage 2L by two different *d*-spacings according to their XRD patterns.⁴² In our XRD patterns, due to the inherent wider peaks in K-ion systems, Fig. S4a and Fig. 3a reveal two continuously shifting and intensifying [002] and [003] peaks of stage 2 from stage 3, suggesting the changes of the *d*-spacing during the formation of stage 2. Together with the *operando* dilatometry discussed above, the electrode thickness evolves nonlinearly during potassiation, suggesting there is a stage 2L phase during potassium intercalation.

***c*-Axis stacking mode.** Regarding the stacking mode during potassiation, the graphite (see its XRD pattern in Fig. S5) features an ABAB stacking sequence, evidenced by the characteristic graphite (101) and (102) peaks. Upon intercalation, forming high-stage GICs, the non-intercalated graphene layers largely maintain their original ABAB stacking sequence, while the regions directly sandwiching the potassium layers may adopt an AA stacking. This transition is quantitatively reflected by the decreasing intensity of the graphite (102) peak in the XRD patterns (Fig. 3c). As the K⁺ concentration increases, the transformation from ABAB to AA stacking within the intercalated regions is progressively completed, with the graphite (102) peak completely disappearing once stage 2 is fully reached. According to the theoretical study, the ABAB stacking mode is beneficial for initial intercalation of K⁺ by lowering the intercalation energy.³⁸ This *c*-axis stacking behaviour, to our best knowledge, is reported for the first time in the K-GICs using experimental methods.



Fig. 4a and Fig. S9 (in SI) show Raman spectra of the low-frequency region and the G band during the first discharge-charge cycle. In graphite, the G band (E_{2g} mode) is one of the



DFT calculations were carried out to understand the K^+ intercalation chemistry based on the low-frequency Raman spectra. There are more than ten Raman active modes in the high-frequency range of 1200–1650 cm^{-1} . These modes are, in general, vibrations of in-plane C atoms with K^+ remaining stationary. Due to large anharmonic effects, standard DFT calculations cannot offer accurate phonon frequencies for high-frequency Raman vibrational modes.^{53–55} Previous DFT work calculated the energy surface of 30 structures for various stages to find the most stable structures.^{7,15} Based on those structures, our DFT calculations show that K-GICs exhibit Raman-active modes in the low-frequency region. We calculated the phonon spectrum for relaxed cells of various stages to find mechanically stable stacking sequences. Our phonon calculations predicted that the stable sequences are $A\alpha A\beta A\gamma A\delta$ stacking for stage 1, $AA\alpha$ stacking for stage 2, and $ABA\alpha$ stack-

Here, we define d_1 as the interlayer distance of graphene layers sandwiching K^+ and d_0 as the intralayer distance without K^+ in between (Fig. S12 in SI). For stages 1–3, the value of d_1 is very close, and d_0 is exclusively determined by the stacking, *e.g.*, AA or AB. This means the sandwich ($\text{A}\alpha\text{A}$ or $\text{B}\alpha\text{B}$) is mostly independent of the other layers. The relative positions of K^+ (noted as α , β , γ , or δ) within graphene layers have a minor effect on the frequency of this Raman active mode. This is due to graphene layers vibrating in opposite directions along the c -axis with K^+ remaining stationary. This indicates the frequency of the mode is dominated by two factors, which are d_0 and d_1 . For example, in stage 3 with stacking sequence $\text{A}\alpha\text{ABA}\alpha\text{AB}$ (Fig. S14 in SI), the A layers vibrate but the B layers remain stationary since only layers sandwiching K^+ vibrate. The frequency of the low-frequency Raman active mode is therefore only influenced by d_1 (5.35 Å, A layer distance), and the effect of d_0 (3.35 Å, AB layer distance) is trivial. For stage 2 with $\text{AA}\alpha\text{AA}\alpha$ stacking sequence, all the A layers vibrate and both d_0 and d_1 influence the frequencies. It has been tested

that even an increase of 0.1 Å in d_0 results in a decrease of 10 cm^{-1} in the frequency. For stage 1, since the K^+ are fully intercalated, all the interlayer distances are defined as d_1 , which dominates the frequency of the mode.

2.5. Electronic changes

To investigate the electronic structure evolution across stages 3 to 1 K-GICs, DFT simulations were performed using structural parameters derived from XRD and Raman spectroscopy. The changes in electronic structure from stage 3 to stage 1, a DFT simulation on charge difference was performed, based on the structural information provided by XRD and Raman analysis. Fig. 5a and Fig. S15 (SI) visualise the charge density difference for three K-GIC stages, where electron accumulation (red isosurfaces) and depletion (blue isosurfaces) are calculated relative to noninteracting K atoms and pristine graphite. The simulations reveal that potassium intercalation progressively

enriches the π orbitals of adjacent carbon rings with electrons. Notably, higher potassium concentrations (*e.g.*, stage 1 KC_8) correlate with greater electron density in the π system, while unoccupied interlayers exhibit minimal charge redistribution.

Experimental validation is achieved using *operando* UV-Vis differential reflectance spectroscopy (DRS), a technique sensitive to electronic band structure changes. As shown in Fig. 5b, the optical response evolves dynamically during cycling: stage-3 KC_{24} absorbs visible light (500–750 nm), appearing dark blue, and stage-2 KC_{16} shows increased reflectance (650–750 nm), appearing orange, while stage-1 KC_8 exhibits increased reflectance (400–750 nm), corresponding to green, yellow, and red wavelengths. Kubelka–Munk analysis^{56,57} of the *operando* UV-Vis spectra (Fig. S15) quantifies the energy gap during potassiation/depotassiation (Fig. 5c). The energy gap increases from near 0 eV (pristine graphite) to 2.4 eV (fully intercalated KC_8) and subsequently decreases during deinter-

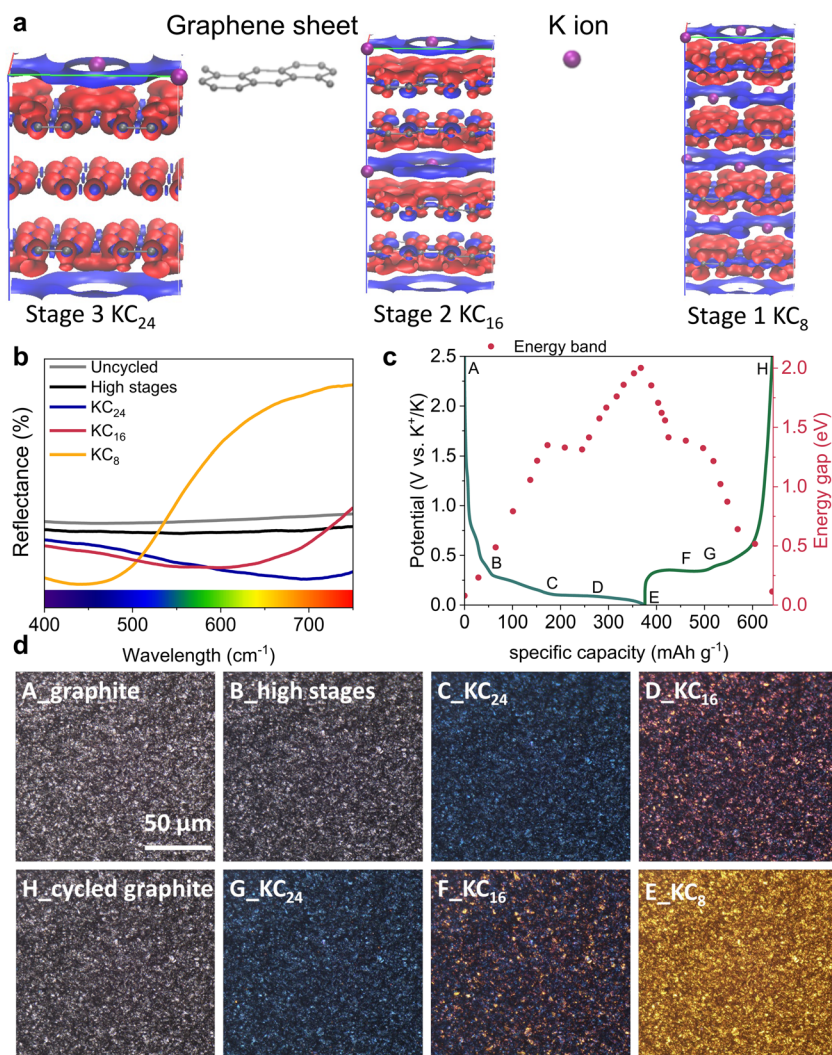


Fig. 5 (a) Charge density difference isosurfaces for stage 3, stage 2, and stage 1 compared with the sum of non-interacting pure C and isolated K systems. The isosurfaces are plotted at $0.0012\text{ electrons Å}^{-3}$, with red positive and blue negative; (b) the UV-visible spectrum (visible range of 400 nm to 750 nm) of uncycled graphite, high stages, K_{24} (stage 3), K_{16} (stage 2) and KC_8 (stage 1); (c) the changes in energy gap (eV) of a graphite electrode during the first potassiation and depotassiation; the A–H are summarised in (d) *operando* microscopy study.



calation. This trend aligns with Fermi level upshifting, which suppresses interband transitions, and only photons exceeding the energy gap are absorbed, while lower-energy light is reflected, explaining the observed colour changes.

In K-GICs, increased potassium concentration delocalises electrons from graphite into the π conduction band (Fig. S16), enhancing metallic behaviour and electronic conductivity.⁵⁸ The same applies to the Li-ion case.⁵⁹ The observed colour evolution of the graphite electrode in Fig. 5d and the Video in SI further corroborates the electronic structure model, as the energy gap modulation directly governs optical properties. This optical behaviour aligns with *operando* UV-Vis DRS and Kubelka-Munk-derived energy gap trends (Fig. 5b and c). The correlation between colour shifts and electronic transitions suggests that simple visible-light monitoring could serve as a cost-effective method to track the status of charge of the graphite anodes in KIBs and beyond. It is noted that some particles can be identified as potassiated (golden colour) while the whole electrode was fully depotassiated, meaning they lose electrical contact with the rest particles or the current collector, leading to a reduction in active material utilisation and also an irreversible expansion of the electrode shown in Fig. 2a.

2.6. Surface chemistry

Apart from the structural and electronic changes of graphite, the surface chemistry can also be tuned by forming a passivation layer, the solid electrolyte interphase (SEI) formed on electrode surfaces from the decomposition products of electrolytes.⁶⁰ The degradation of a graphite electrode, caused by large volume change, can lead to particle fracture and loss of network connection,⁶¹ which can further result in electrode delamination, exfoliation, and vulnerable SEI cracking. Each of these steps contributes to capacity loss by depleting the active potassium inventory of the cell.³⁴ XRD and dilatometry analysis both indicate large volumetric variations in both atomic and electrode-level scales. The continuous “breathing” of the graphite particles can cause the SEI layer to crack and rupture, exposing fresh graphite surfaces to the electrolyte. This triggers further electrolyte decomposition and SEI reformation, consuming active potassium and electrolyte, and leading to increased impedance.¹⁰ Therefore, a robust SEI layer is essential to ensure stable cycling and alleviate battery degradation. The formation of a passivating SEI layer protects the graphite lattice physically, suppresses further decomposition of the electrolyte,⁶² and facilitates the diffusion of ions.⁶³ To characterise this layer from a cycled graphite electrode, *ex situ* time-of-flight secondary ion mass spectrometry (ToF-SIMS) was employed.

It is documented that the SEI derived from the most common KPF₆ electrolyte is the decomposition of solvents, resulting in an organic-rich SEI layer; while the SEI on the graphite electrode with KFSI-based electrolyte is predominantly composed of inorganic compounds, originating from the decomposition of KFSI salt.¹³ Given the increased use of KFSI-based electrolytes in the battery community,³² this salt has received more research interest due to its stable SEI and improved cycling performance.

According to ToF-SIMS data (Fig. 6a, b, and Fig. S17 in SI), the depth profiles of different species were revealed for both C-containing, O-containing, and S-containing species, and F-containing species. As the SEI layer was thin (with a thickness of 2.0 nm–3.0 nm from Fig. 6c), only a Bi⁺ analysis beam was used to observe the subtle change in the SEI layer. Fig. 6b shows the depth profiles of the SEI layer, focusing on various F-containing species (such as KF[−], SF[−], and CF[−]) across the surface, from the surface to the inner SEI layer to the bulk graphite. The analysis revealed a decreasing trend in F-containing species from the surface to the inner phase of the SEI until it reaches a plateau. While it is true that F contaminations are prevalent in most ToF-SIMS analyses conducted in negative mode due to their ubiquity and high electron affinity, we took extra care in our experimental procedures to minimise this effect. Thus, it is unlikely that the high F[−] signal only results from surface contamination. Instead, it is plausible to deduce that F plays a significant role in the SEI. Moreover, other F-containing species like KF₂[−], SF[−], and CF[−] provide complementary evidence that a higher concentration of these species is present in the outer SEI compared to the inner layers. These reduction products of the KN(SO₂F)₂ salt would be a key factor to demonstrate stable SEIs on the graphite surface.⁶ On the other hand, Fig. 6a shows the depth profiles of the C-containing species such as CO[−], C₂H[−] and CO₃[−] across the graphite surface. According to the analysis, C-containing species were concentrated in the inner layer of the SEI. In addition, Fig. 6a shows the depth profile of S-containing species. It is reported that, in KIBs, sulfites could easily accept electrons from the solvents and prevent solvents and K⁺ co-intercalation into the electrode material, in comparison to the oxygen-containing species.⁶⁴ An increase in the concentration of C-containing species and S-containing species can be observed from the surface towards the inner layer until it reaches a plateau where the SEI is sputtered.

It is well-documented that the N(SO₂F)₂[−] anion can result in a robust⁶⁵ but thin SEI layer (less than 10 nm) with an F-containing, specifically KF-rich⁶⁶ protective inorganic layer because of N(SO₂F)₂[−] decomposition.^{67,68} It is reported that KF[−] components can effectively prevent the co-intercalation of solvated K-ions, enabling stable cycling.⁶⁹ In the KFSI in EC/DEC system, it is more likely that the organic phase within SEI is formed by the reduction of the solvent molecules, while S-containing species and F-containing species were formed from anions (N(SO₂F)₂[−]). It was hypothesised that the inorganic and organic components represent the flexibility of the SEI layer, while the inorganic elements represent its rigidity.^{70,71} Fig. 6c schematically shows the SEI on a graphite anode according to ToF-SIMS analysis, and the structure of the SEI layer is also in good agreement with previous findings.⁷² Especially in KIBs, these flexible organic SEI components can be useful in accommodating the large volume expansion during cycling.⁷² Hence, an organic inner layer with an F-concentrated protective passivated surface could be beneficial to enhance the surface stability for long cycling by preventing excessive depletion of the potassium inventory in the system.



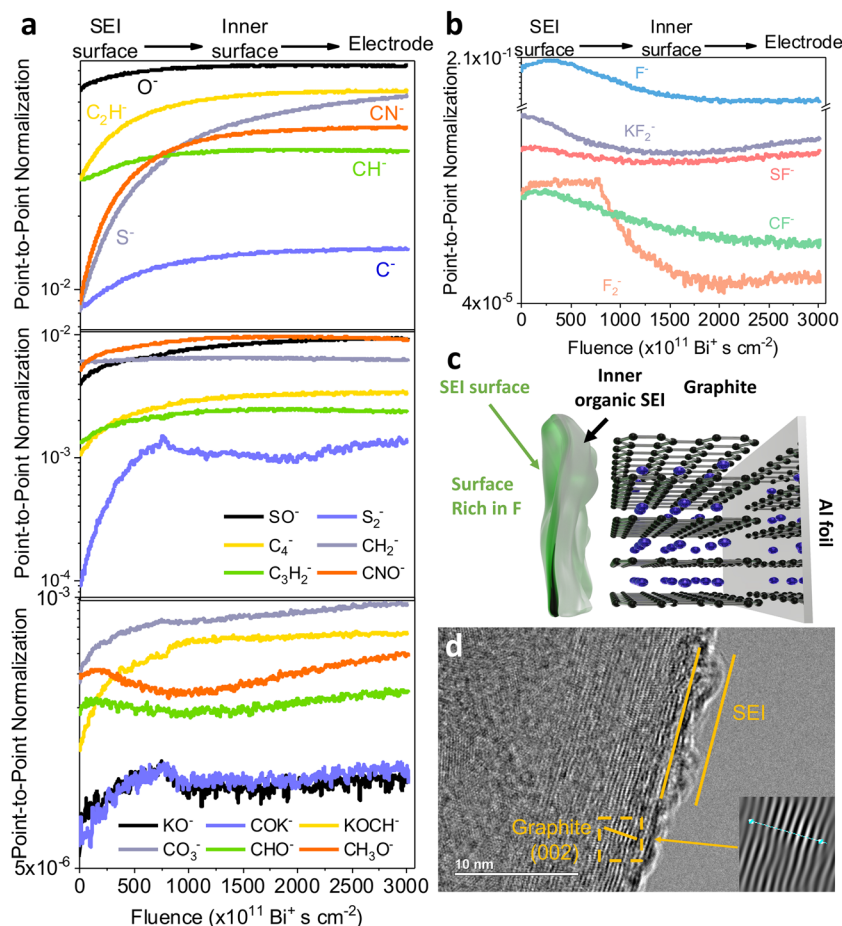


Fig. 6 *Ex situ* ToF-SIMS depth profiling (using Bi^+ primary ion beam only) in the graphite electrode (a) for C-containing, O-containing, and S-containing species, and (b) for F-containing species. All the data are point-to-point normalised to total counts; (c) the schematic diagram of the KFSI-derived thin SEI layer on graphite; (d) an *ex situ* TEM image of the cycled graphite after the first cycle.

To visualise both the thickness of SEI and the d -spacing of the cycled graphite, *ex situ* TEM was also carried out. Fig. 6d shows that the thickness of the as-formed SEI ranges from 2.0 to 3.0 nm after the first cycle compared with the TEM image of pristine graphite (Fig. S18 in SI). The crystallinity of the cycled graphite is inferior to pristine graphite; these findings confirm that K^+ intercalation disrupts long-range graphite order, favouring disordered lattice rearrangement.

3. Conclusion

A series of *operando* characterisation methods was used to elucidate the structural, electronic, and chemical changes induced by electrochemical potassiation/depotassiation in graphite. *Operando* synchrotron XRD and electrochemical dilatometry confirmed the theoretical c -axis expansion of 60% at full potassiation from graphite compared to a 49% expansion at the electrode level. Synchrotron XRD and Raman spectroscopy together with DFT calculations provide stacking information as follows: from pristine graphite to stage 1 KC_8 through liquid-like stages (stage 10L $\rightarrow$ 9L $\rightarrow$... $\rightarrow$ 4L) followed

by in plane ordered ($p(2 \times 2)R0^\circ$) stages (KC_{24} stage 3 $\text{ABA}\alpha$, KC_{16} stage 2 $\text{AA}\alpha$) before reaching the final stage 1 KC_8 ($\text{A}\alpha\text{A}\beta\text{A}\gamma\text{A}\delta$). We also identify the existence of stage 2L between stage 3 and stage 2. UV-vis spectroscopy and optical measurement revealed that the intercalation of potassium leads to an upshifted Fermi level of graphite, as more electrons flow into π orbitals. This change leads to the optical properties, with stage 1 gold KC_8 , orange stage 2 KC_{16} and blue stage 3 KC_{24} . *Ex situ* ToF-SIMS explained the superior surface chemistry of the SEI structure, that the outer SEI layer is rich in F-containing species, while the inner SEI layer is more organic. Our results provide a comprehensive fundamental understanding of K^+ intercalation, revealing the K^+ storage mechanism in graphite and opening the paths towards further investigation of the K-GICs chemistry.

Author contributions

Conceptualisation: MT and ZG; supervision: MT; formal analysis: ZG, MT, KW, YZ, C. Molteni, PDH, and FX; funding acquisition: MT; investigation: ZG, YZ, GC, YH, CW, ZS, JJ; method-



ology: ZG, MT; software (DFT simulation): KW, C. Molteni, and PDH; visualisation: ZG and KZ; writing – original draft: ZG, KW and YZ; writing – review & editing: all authors.

Conflicts of interest

The authors declare that they have no competing interests.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary information (SI). The SI incorporates experimental details, graphite characterisation, operando spectra (XRD, Raman, and UV-vis), and simulated K-GIC structures. See DOI: <https://doi.org/10.1039/d5eb00184f>.

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