

Tuning surface chemistry to reduce the step-like degradation of LiCoO₂ at 4.6 V

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ABSTRACT

Elevating the cut-off voltage is an effective route to increase the energy density of LiCoO₂ (LCO). However, the highly delithiated LCO faces the issues of poor structural reversibility, O loss, and Co dissolution, etc., especially in the surface region. Herein, the step-like surface degradation (SSD) of pristine LCO (P-LCO) is firstly revealed to be responsible for the rapid capacity decay. To reduce the adverse impact of SSD, a solid electrolyte is coated and annealed to achieve the optimized surface structure chemistry of LCO (SE-LCO), featuring the outermost surface Li₃PO₄, surface rock-salt layer, and subsurface spinel-like layer. Benefiting from this surface optimization, the SE-LCO not only shows an enhanced but more reversible phase transition to enhance the structure stability, but also promotes the formation of tough cathode electrolyte interface (CEI) to reduce the O loss and Co dissolution issues. As a result, SE-LCO/graphite cell achieves excellent cycle stability with a remarkable capacity retention of 81.2% after 800 cycles in a potential range of 3–4.55 V, which is among the best reported cell performances. This work broadens the cognition for developing more advanced LCO cathodes.

1. Introduction

In the past decades, lithium-ion batteries (LIBs) have become an indispensable part of our daily lives and are widely used in portable electronic devices, electric vehicles, and stationary energy storage [1–3]. Among the cathodes available on the market, LiCoO₂ (LCO) occupies most of the market in the field of consumer electronics products due to its outstanding conductivity and high volumetric energy density [4]. However, with the increase of energy consumption and the expansion of market scale, higher requirements are put forward for the energy density of batteries. Elevating the upper cut-off voltage is an effective route to achieve higher energy density. When the charge cut-off voltage increases to 4.6 V vs. Li/Li⁺, the discharge capacity of LCO can reach about 220 mAh g⁻¹, which is a great improvement comparing with the currently used LCO at 4.45 V (about 173 mAh g⁻¹) [5].

However, operating at such a high voltage, LCO faces a series of issues that lead to rapid capacity decay. 1st, when the voltage is higher than 4.55 V vs. Li/Li⁺, the irreversible phase transition from O3 to H1–3

occurs, which is accompanied by a drastic volume change, resulting in the slippage of Co-O layers and formation of micro-cracks [6–8]. 2nd, the overlap between Co_{3d} and O_{2p} bands with high delithiation state leads to part of the lattice O participating in the charge compensation and forms the oxygen redox (O^α, 0 < α < 2), resulting in O loss and irreversible phase transition (CoO₂ → Co₃O₄) [9]. Last but not least, the highly oxidative Co⁴⁺ and O^α on the surface of LCO can react with the organic components in the electrolyte, leading to side reactions and formation of undesired cathode electrolyte interphase (CEI) [10]. It is worth noting that the delithiation state in the surface is much higher than in the bulk due to the gradient distribution of Li⁺ inside the LCO after charging [11]. Jiang et al. reported that physical strain effect can initiate massive cracks on the surface of LiCoO₂, which aggravates chemical effects such as etching, corrosion and side reactions [12]. The previous report of our group has revealed that, the curvature of Co-O layers occurring near the surface dictates the structural stability of LCO at high potentials [13]. Therefore, the high-voltage issues are more serious on the surface of LCO, and surface optimization is considered to

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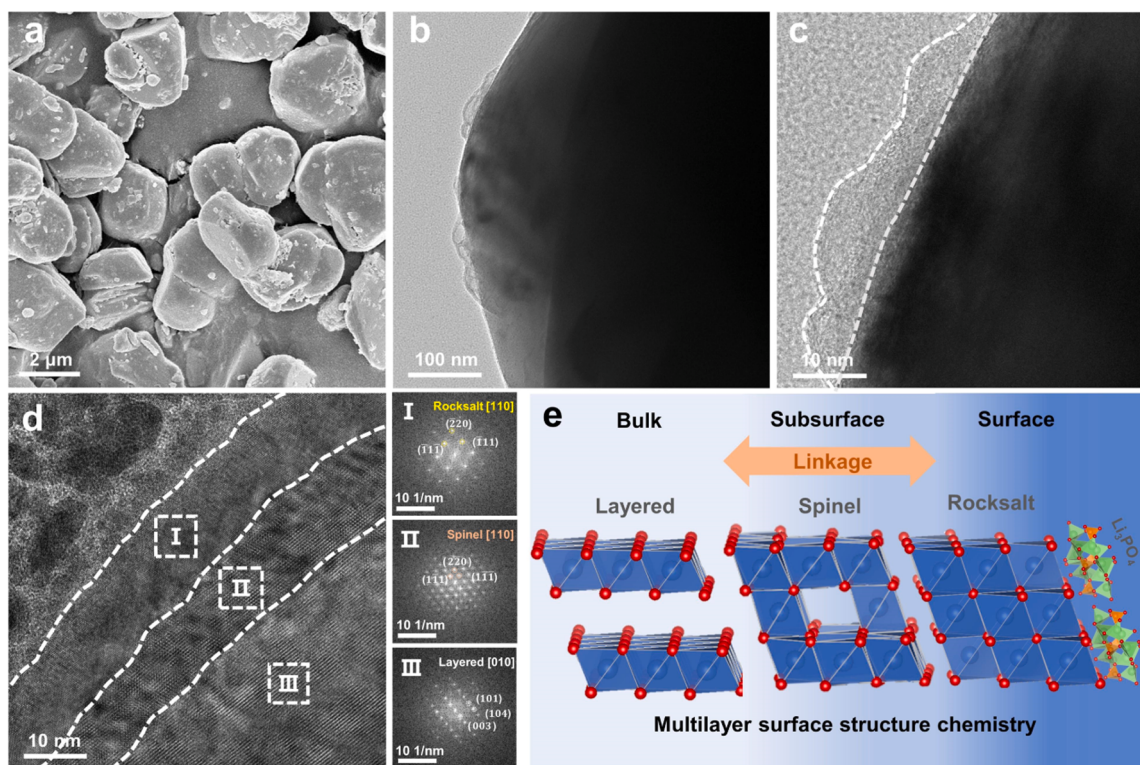


Fig. 1. Material characterization. (a,b) SEM and TEM morphologies of SE-LCO particles (entire particles without cutting treatment by FIB). (c) Morphology of surface Li_3PO_4 . (d) Surface and subsurface structures, and diffraction pattern analyses. (e) Schematic illustration of surface structure of SE-LCO.

be an effective mean to enhance the stability of LCO at 4.6 V.

According to the above analyses, to achieve better cycle stability, a reasonably optimized surface structure chemistry with the following characters is needed: 1st, the surface structure must be strong enough with a high mechanical/ chemical stability to resist the repeated high-voltage volume variations; 2nd, it must effectively isolate the electrolyte from LCO, and reduce the occurrence of side reactions; 3rd, the oxygen framework must be stabilized to reduce the O loss from surface. In the past decades, various approaches have been developed to strengthen the surface of LCO for prolonged cycle lifespan. Using metal oxides and fluorides as physical barriers can avoid the direct contact between the cathode and electrolyte [14,15]. However, these coatings will increase the surface impedance and worsens the transport kinetics of Li^+ . Phosphate coatings can promote Li^+ -ion's transport and reduce the side reactions, but the coating is not strong enough to bind with the LCO surface due to the structural incoherency [16,17]. Recently, the spinel phase layers acting as the surface structure layer have been heavily reported, which not only provide a channel for faster Li^+ -ion's transport, but also stabilize the surface lattice O attributing to the more stabilized oxygen framework [18–21]. Some researchers have pointed that the high-entropy rock-salt (RS) shell can effectively suppress the O loss and near-surface structure destruction [22]. The solid electrolytes, including the $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$, $\text{Li}_{1.8}\text{Sc}_{0.8}\text{Ti}_{1.2}(\text{PO}_4)_3$, etc., are massively reported to react with LCO surface upon annealing, and form a surface spinel phase layer [23,24]. Meanwhile, high-entropy surface shell may be formed due to the presence of plentiful elements. Despite the above advances, the relevant optimizing mechanism is still in debate, which blocks the further development of high voltage LCO cathodes.

In this work, we first reveal the step-like surface degradation (SSD) of P-LCO at 4.6 V, which is highly related to the rapid capacity decay. Then, to reduce the adverse impact of SSD, a solid electrolyte ($\text{Li}_{1.3}\text{Al}_{0.1}\text{Ti}_{1.9}\text{Si}_{0.2}\text{P}_{2.8}\text{O}_{12}$) is coated and annealed to achieve the optimized surface chemistry of LCO (SE-LCO), featuring the outermost

surface Li_3PO_4 , surface RS layer, and subsurface spinel-like layer. The benefiting roles are as follows, 1st, this surface chemistry optimization can not only improve the homogeneity of Li^+ extraction, but also serves as a hard shell effectively avoiding the generation of surface step-like degradation. 2nd, it stabilizes the near-surface lattice O and inhibits the Co dissolution, reducing irreversible phase transition from layer to spinel on the surface of LCO. In addition, this optimized surface chemistry can inhibit the occurrence of side reactions and promote to form a uniform and stable LiF-rich CEI. Benefiting from these advantages, the SE-LCO/graphite cell achieves an excellent cycle stability with a remarkable capacity retention of 81.2% after 800 cycles in potential range of 3–4.55 V, which is among the best reported cell performances. This work reveals a novel step-like surface degradation of layered cathodes operating at high-voltage, and provides new insights for developing the more advanced cathode materials for LIBs.

2. Result and discussion

2.1. Material characterizations of SE-LCO

The utilization of solid electrolytes as coating materials has been massively reported to enhance the cycle stability of LCO upon high voltages [23–28]. Here, we select the commercialized solid electrolyte (i.e., $\text{Li}_{1.3}\text{Al}_{0.1}\text{Ti}_{1.9}\text{Si}_{0.2}\text{P}_{2.8}\text{O}_{12}$) as the coating material, which contains plentiful foreign elements (Al, Ti, and Si) and inert polyanion (PO_4^{3-}) to optimize the surface chemistry of LCO. A commercialized LCO is selected as the pristine LCO (P-LCO), featuring with pure layered structures in both the surface and bulk regions (Fig. S1). The LCO coating process is achieved via a high energy ball milling, then follows with a high-temperature annealing (Fig. S2). The mass ratio of LCO to solid electrolyte is 50/1. More detailed synthesis process is described in the experimental section (Supporting information).

To obtain the optimum annealing temperature, three annealing temperatures are selected, including 600, 700, and 800 °C. The

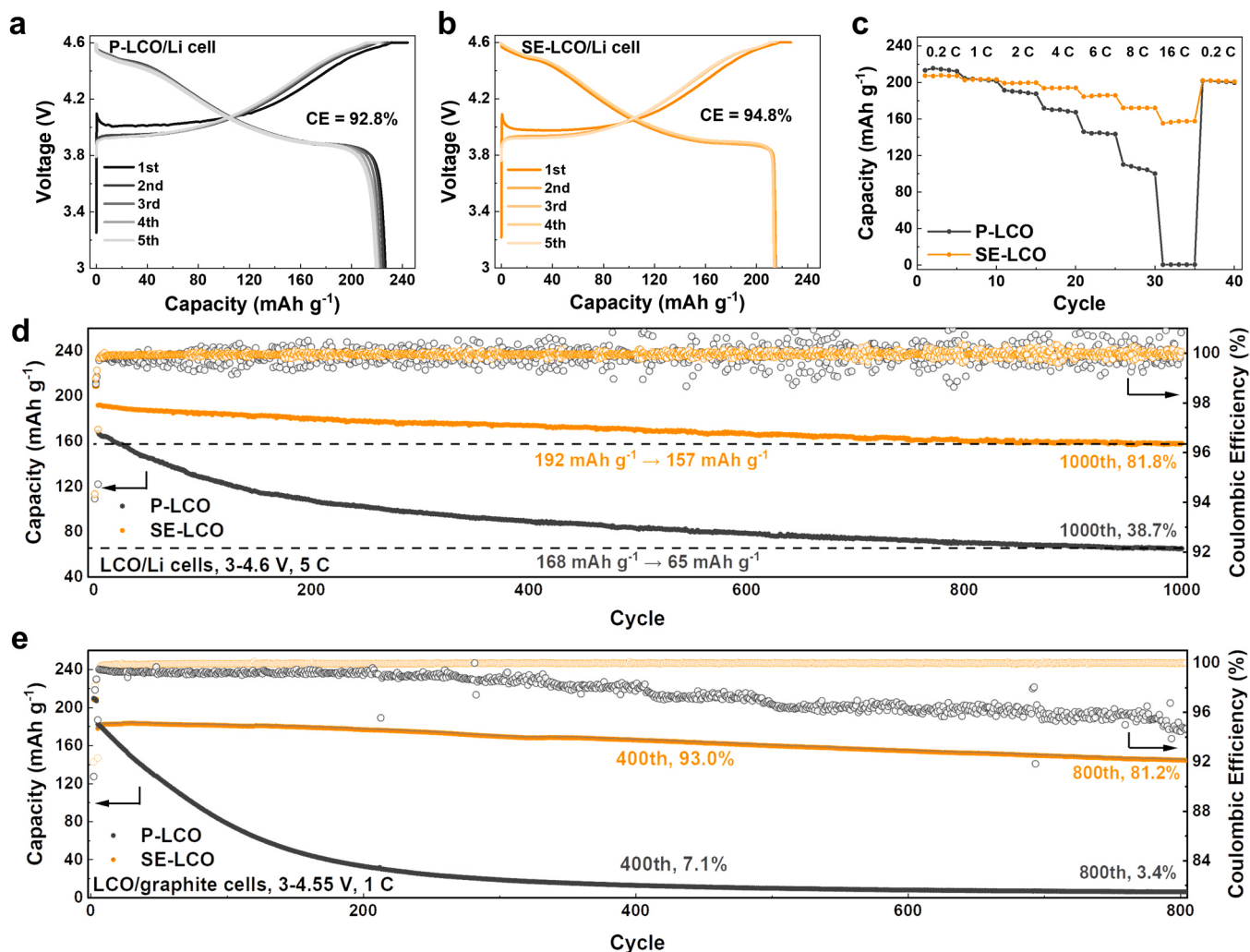


Fig. 2. Cell performances. (a,b) Charge/discharge curves in initial 5 cycles at current of 0.2 C. (c) Comparison of rate performances. (d,e) Comparison of cycle stability of P-LCO and SE-LCO in LCO/Li cells in 3–4.6 V and at current of 5 C, and in LCO/graphite cells in 3–4.55 V and at current of 1 C.

morphology evolution of LCO products during synthesis is illustrated in Fig. S3, and the X-ray diffraction (XRD) patterns of LCO products and the correlated cycle performances of the LCO/Li cells are shown in Fig. S4, S5. These results indicate that, the phase composition of LCO products under three annealing temperatures are basically the same, and the cells using LCO cathode annealed at 700 °C show the best cycle stability. Therefore, in this work, the LCO product annealed at 700 °C is named as the SE-LCO, and is selected as the main object of study to reveal the benefiting roles of the optimized surface chemistry. The morphology of SE-LCO is shown in Fig. 1a, showing the homogeneous surface coating on SE-LCO.

Generally, upon annealing, the chemical reactions between the coated solid electrolyte and LCO mainly occur on the surface rather than in the bulk region. That is, the layered structure in the bulk region can not be affected by the coating process. As shown in Rietveld refinement results of XRD patterns (Fig. S6, Table S2, S3), SE-LCO displays the same *R-3m* layered structure with P-LCO, indicating that the surface coating has little influence on the bulk structure of SE-LCO. The complicated chemical reactions between the solid electrolyte and LCO lead to the rearrangement of element distribution and crystal structure in the surface of LCO. X-ray photoelectron spectroscopy (XPS) is utilized to probe the element distribution in the surface region (Fig. S7). The results illustrate that, the Si and P mainly enrich in the outermost surface region, while the Ti and Al are able to diffuse into the surface Co-O framework of LCO. Further fitted results of the XPS O 1s spectra

identify the existence of Ti-O, P-O, and Si-O bonds in the surface of SE-LCO (Fig. S8).

The surface morphology of SE-LCO is characterized using transmission electron microscopy (TEM), in which the powder of SE-LCO is directly placed on a copper grid, without any cutting treatment by the focused ion beam (FIB), as shown in Fig. 1b,c. It can be observed that the outermost surface deposits are about tens of nanometers in the size and about 5–10 nanometers in the thickness, and discontinuously distributed on the surface of SE-LCO. Upon more subtle observation, these surface deposits are in a short-range ordered state or near amorphous state, as analyzed from the diffraction plots in Fig. S9. The diffraction pattern results further refer that, the surface deposits are mainly composed of Li₃PO₄ with different orientations in an *Pcmn* space group. The existence of Li₃PO₄ is considered to play a significant role on regulating the property of cathode electrolyte interface (CEI) for the promoted Li⁺ transport and the reduced side reactions [7,25,29–31]. Besides, the weaker peak of C=O/O=C=O in XPS C 1s spectra of SE-LCO indicates that the Li₂CO₃ impurities can be effectively removed during the annealing process (Fig. S10), which is beneficial for the manufacturing of electrodes.

Besides the surface Li₃PO₄ deposits, the surface structure of LCO is also regulated. To probe the cross-section surface structure, the SE-LCO particle is firstly sliced and thinned by FIB, and then characterized by TEM. As shown in Fig. 1d, SE-LCO exhibits a unique multilayer structure, composing of the surface rocksalt (RS) layer, the subsurface spinel-

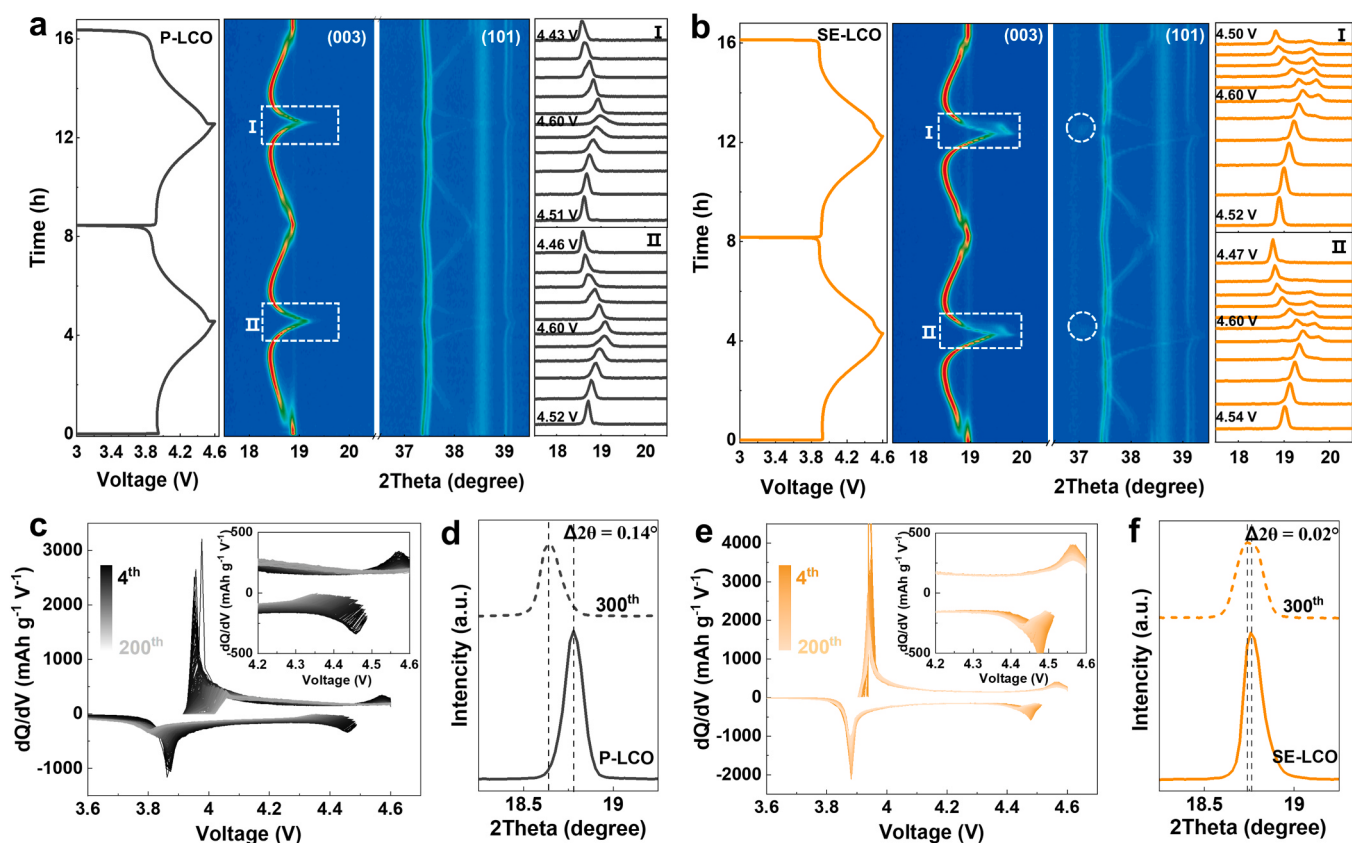


Fig. 3. The reversibility of phase transitions. (a,b) The *in-situ* XRD patterns of P-LCO and SE-LCO in initial two cycles. (c,e) The dQ/dV curves in 200 cycles. (d,f) Variations of (003) peaks of two samples between the pristine and after 300 cycles.

like layer, and then the adjacent layered structure in the bulk. Combining with the TEM-EDS analyses in Figure S11, we further obtain the element distribution of this optimized surface structure. The formation of surface RS layer is mainly attributed to the introduction of Al, Ti, and Si elements, which forms a high entropy region to stabilize the surface structure of SE-LCO [15,22]. Meanwhile, the formation of surface RS layer is accompanied with O loss, which can be verified by the thermo-gravimetric analysis (TGA) results (Fig. S12). Below this RS layer, the subsurface spinel-like phase layer is a Ti-rich spinel phase, which acts as a linkage between the surface RS layer and the bulk layered structure, alleviating the lattice mismatch between the two layers. The introduction of Ti in the spinel phase not only helps to enhance the Li⁺ diffusion kinetics, but also serves as an oxygen stabilizer due to the formation of more stable oxygen framework [19,21,32]. Based on the above results, we obtain a clear understanding on the structure chemistry in the surface region of SE-LCO, and the correlated schematic diagram is shown in Fig. 1e. The excellence of the surface chemistry of SE-LCO mainly lies in the synergistic effect of multiple structures, including the outermost surface Li₃PO₄ deposits, the surface RS layer, and the subsurface spinel-like layer, which play a significant role on both stabilizing the surface structure and reducing the side reactions.

2.2. Cell performances

The cell performances of the LCO/Li cells are firstly evaluated in a potential range of 3–4.6 V. Fig. 2a,b show the charge/discharge curves of P-LCO/Li and SE-LCO/Li cells at a current of 0.2 C (1 C = 200 mA h g⁻¹). The discharge capacity of P-LCO decreases rapidly in the initial cycles, indicating the serious structural degradation occurs in the initial cycles. On the contrary, the discharge curves of SE-LCO are well overlapped in the initial cycles, showing a much better stability than P-LCO.

Furthermore, the SE-LCO presents a higher initial coulomb efficiency (ICE) than P-LCO, indicating less side reactions between the cathode and electrolyte. We further conduct the rate performance tests, as shown in Fig. 2c. The SE-LCO presents a excellent discharge capacity of 157.6 mA h g⁻¹ at 16 C, which is much superior to P-LCO, mainly due to the optimized surface chemistry.

The cycle performances are also conducted to evaluate the effectiveness of the optimized surface chemistry. Fig. S13 compares the cycle performances of P-LCO/Li and SE-LCO/Li cells at a current of 1 C. The results indicate that, the SE-LCO/Li cell shows a high capacity retention of 89.1% after 300 cycles at 1 C, while for the P-LCO/Li cell, the capacity retention in 300 cycles is only 37.8%. The comparison of cycle performances of the P-LCO/Li and SE-LCO/Li cells at a current of 5 C is also presented in Fig. 2d. The SE-LCO/Li cell delivers an initial capacity of 192 mA h g⁻¹, and a remarkable capacity retention of 82.5% after 1000 cycles at 5 C, while for P-LCO/Li cell, the initial capacity is 168 mA h g⁻¹, and the capacity retention after 1000 cycles is only 38.4%. Further, the cycle performance of SE-LCO/Li cell at 45 °C and at 1 C is also significantly better than that of P-LCO/Li cell, as shown in Fig. S14.

From a more practical aspect, we further examine the durability of SE-LCO in LCO/graphite full cells. The potential range is selected as 3–4.55 V, which equals to the potential range of 3–4.6 V in LCO/Li cells. As shown in Fig. 2e, the SE-LCO/graphite cell demonstrates an excellent cycling performance, which exhibits capacity retention of 93.0% and 81.2% after 400 and 800 cycles at 1 C, respectively. In contrast, P-LCO/graphite cell only remains a low capacity retention of 7.1% after 400 cycles at 1 C. To the best of our knowledge, this cell performance is quite competitive among the reported cells using high-voltage LCO cathodes (Table S4). Overall, due to the optimized surface chemistry, the SE-LCO presents excellent cycling stability and rate performance.

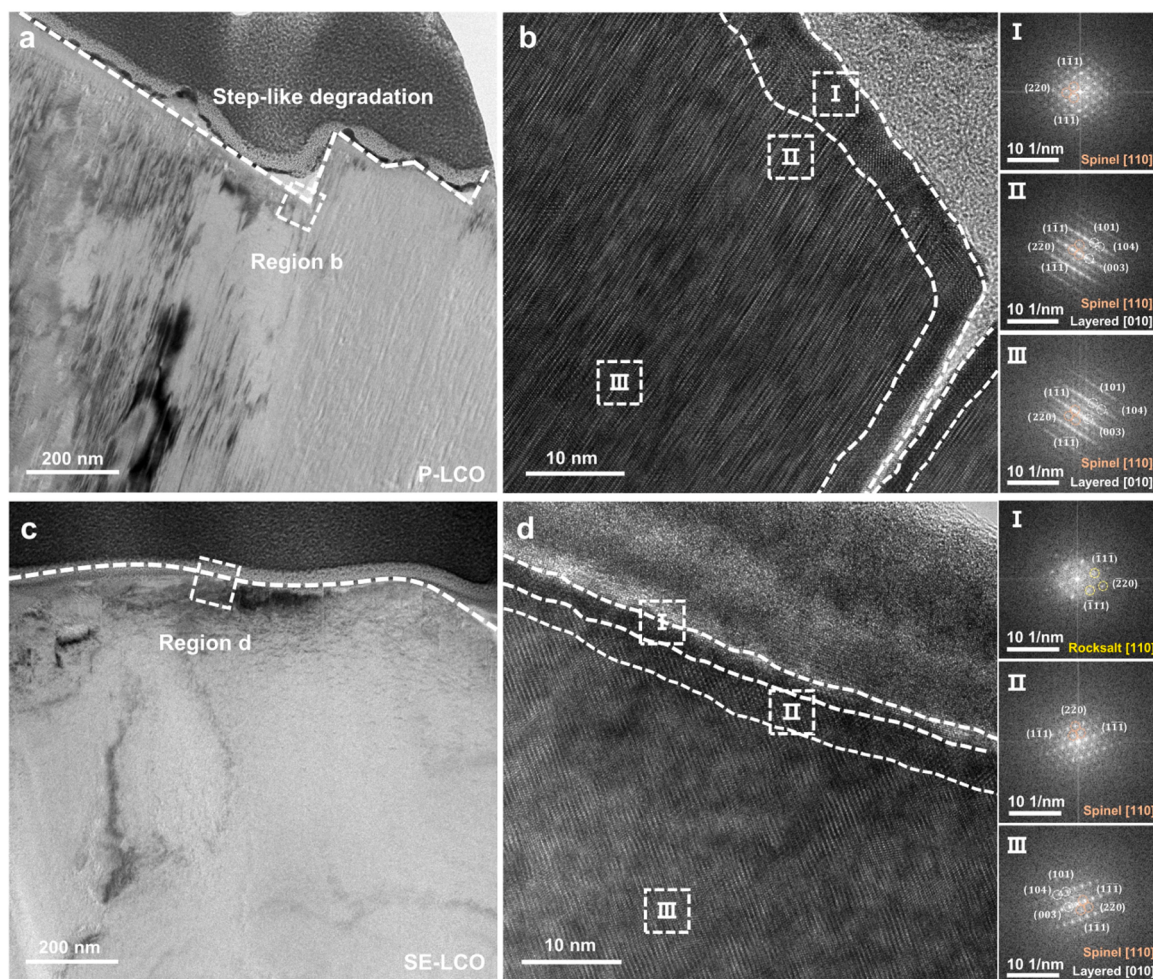


Fig. 4. Revealing the step-like surface degradation at the charged state in the 1st cycle. (a) TEM characterization of the step-like surface degradation for P-LCO, and (b) the corresponded surface structures and related diffraction pattern analyses. (c) TEM characterization of the smooth surface for SE-LCO, and (d) the corresponded surface structures and related diffraction pattern analyses.

2.3. Enhanced phase transition reversibility

To make the enhanced cycle stability clear, we first analyze the optimized phase transition reversibility via multiple characterizations, including *in-situ* XRD, TEM, dQ/dV curves, etc. It has been massively reported that the O3/H1-3 phase transition beyond 4.55 V is detrimental for the cycle stability of LCO cathodes [6–8,33,34]. In order to probe the detailed structure evolution upon cycles, the *in-situ* XRD measurements are employed in a potential range of 3–4.6 V and at a low current of 50 mA g⁻¹. In general, the variation of (003) peaks locating at the 2θ of around 18.9° is associated with the change of layer spacing along the c-axis, serving as a sensitive indicator for phase transition [35, 36]. As shown in Fig. 3a,b, we observe that the changes of (003) peaks of P-LCO and SE-LCO are similar in 3–4.5 V, indicating the similar phase transition at voltage below 4.5 V. When the voltage is elevated to above 4.5 V, new peaks around 19.6° and 37.1° are observed in the XRD patterns of SE-LCO, which are not clear in P-LCO. In Fig. S15a,b, we compare the (003) peaks of P-LCO and SE-LCO at 4.6 V. The (003) peaks can be further divided and fitted into three peaks, including pure O3, O3/H1-3 intergrowth, and pure H1-3, locating at 2θ of 18.8°, 19.2°, and 19.6°, respectively [37]. The higher proportion of O3/H1-3 intergrowth and H1-3 phases in SE-LCO indicates that more H1-3 phase transitions occur in SE-LCO comparing with P-LCO, which can be further reflected in the dQ/dV curves in *in-situ* XRD measurement (Fig. S15c,d). Since the Li content extracted from the P-LCO is slightly higher than that from SE-LCO, P-LCO shall be more inclined to undergo the O3/H1-3

phase transition. However, the experimental result is not in line with this hypothesis. We assume that, for P-LCO, when charged to above 4.5 V, for the major Li-O layers in the bulk, the delithiation content is not enough to drive the O3/H1-3 phase transitions, while for some minor Li-O layers, the delithiation content is too large to cause the irreversible slip of Co-O layers, leading to the formation of step-like surface degradation. As reflected in the *in-situ* XRD characterizations, the O3/H1-3 phase transitions in P-LCO are lesser than in SE-LCO.

The more reversible phase transition behavior can also be further reflected in dQ/dV curves, especially in the high voltage range of 4.45–4.6 V. As shown in Fig. 3c,e, the redox peaks in dQ/dV curves locating at the range of 4.45–4.6 V in 200 cycles are more reversible than that of P-LCO, demonstrating the higher phase transition reversibility. Besides, the comparison of *ex-situ* XRD patterns between the electrodes at fresh state and after 300 cycles are utilized to reveal the more reversible phase transitions in SE-LCO. As shown in Fig. 3d,f, and Fig. S16, the (003) peak variation amplitude of SE-LCO after 300 cycles is just 0.02°, which is obviously weakened than that of P-LCO (about 0.14°), demonstrating the more stabilized phase structure of SE-LCO upon long-term cycles. The above results indicate that the more reversible phase transition can be achieved via optimizing the surface chemistry. In other words, optimizing the surface chemistry can not only enhance the surface stability, but also strengthen the bulk structure reversibility.

The cross-section TEM characterizations are further performed to reveal the mechanism for the more reversible phase transitions of SE-

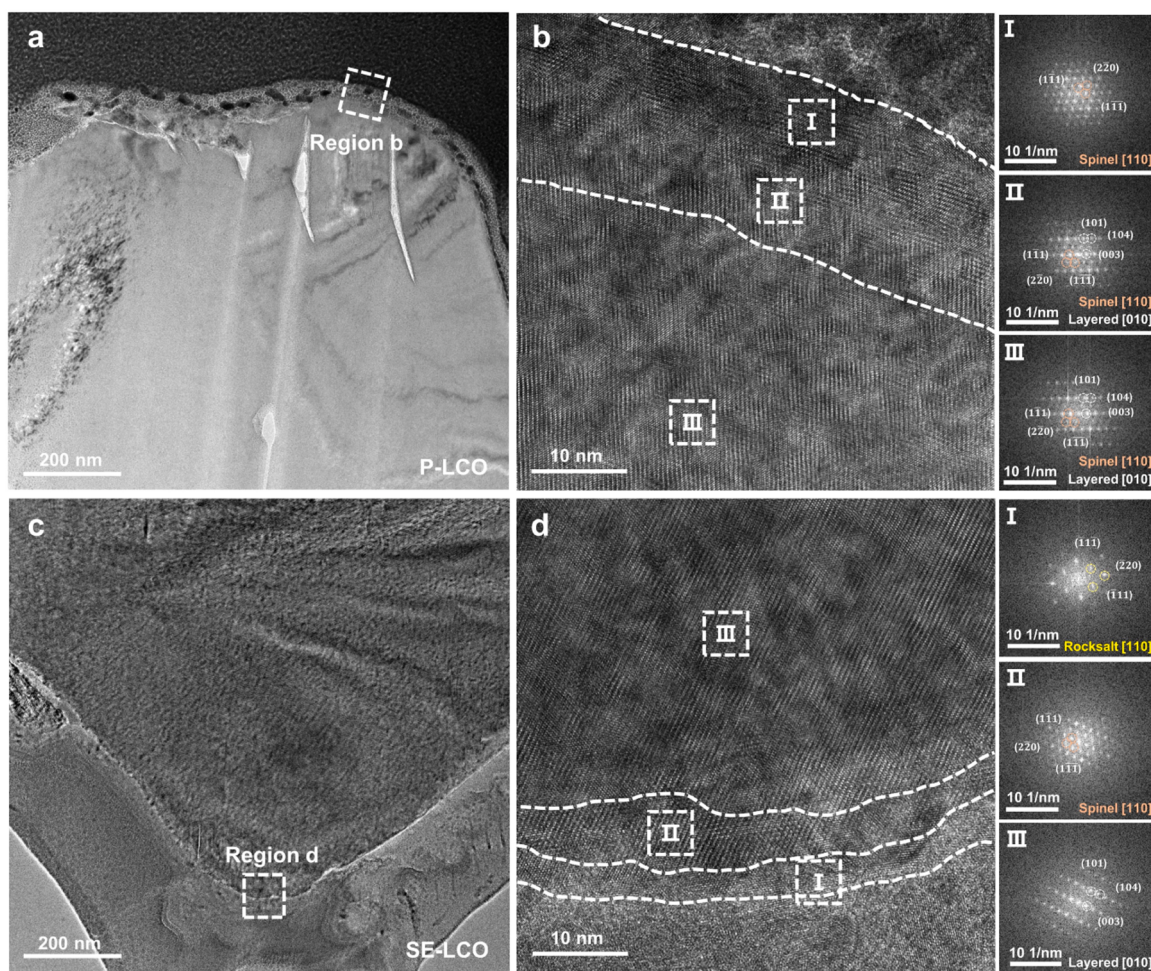


Fig. 5. Surface structure deterioration after long-term cycles. TEM characterization of (a) the surface morphology of P-LCO, and (b) the correlated surface structures and corresponding diffraction patterns. TEM characterization of (c) the surface morphology of SE-LCO, and (d) the correlated surface structures and corresponding diffraction patterns.

LCO, as shown in Fig. 4. As shown in Fig. 4a,c, and Fig. S17, when charged to 4.6 V in the 1st cycle, a severe step-like degradation morphology with a few micro-cracks is observed in the surface of P-LCO, while for SE-LCO, no noticeable step-like degradation is observed. The occurrence of this step-like degradation of P-LCO is speculated to be attributed to the uneven Li^+ -ion extraction from the surface. In other words, for P-LCO, the Li^+ -ions are extracted in some localized surface region upon charge, rather than homogeneously extracted from the overall surface, which makes some of the Li layers are in over-delithiated state, and thus leading to the severe and irreversible slip of the Co-O slabs, and also causing the step-like surface degradation.

This step-like surface degradation can be further confirmed by surface structure analyses. Upon more subtle observation via TEM, for P-LCO, the surface structure nearby the step-like region has transformed to a typical spinel-like phase, with a spinel/layer hybrid structure in the beneath region (Fig. 4b). What's more, serious lattice distortions are shown in both the subsurface regions II and III, as confirmed by the streaked reflections in diffraction patterns, indicating the lattice distortions due to the over-delithiation in these regions. Fig. S18 further shows the surface structure in the “non-step” surface region, although the surface region also features a surface spinel-like structure and a subsurface spinel/layer hybrid structure, the degree of lattice distortions are significantly lower than that nearby the step-like surface regions. The difference in surface structures of two regions also illustrates the uneven Li^+ -ion's delithiation behavior from surface of P-LCO. In contrast, for SE-LCO, the surface structures are basically the same as the

pristine sample (Fig. 4d), and no lattice distortions can be observed in the subsurface region. The result indicates that optimizing surface chemistry can effectively avoid the surface damage caused by the formation of step-like surface degradation.

According to the above results, we speculate that the poor cycle stability of P-LCO and the correlated weaker O3/H1-3 phase transition are closely related to the appearance of step-like surface degradation. For P-LCO, due to the uneven Li^+ -ion's delithiation from surface, upon charge to 4.6 V, some Li-O layers (in minority) are in over-delithiated state, while other Li-O layers (in majority) are in less-delithiated state. As a result, the step-like surface degradation generates due to the over-delithiation in these step-like regions, mainly due to the irreversible slip of the Co-O layers. Due to the formation of step-like surface degradation, some fresh Co-O slabs are exposed to electrolyte, and thus a series of issues occurs including the micro-cracks, lattice oxygen loss, and side reaction, etc., which further exacerbates the deterioration of electrode performances. As for SE-LCO, the optimized surface chemistry not only makes Li^+ -ion's deintercalation more homogeneously, but also acts as a hard shell to maintain the reversible slip of Co-O layers upon charging to the high voltage of 4.6 V, thus avoiding the appearance of step-like surface degradation. Even if there exists some slight lattice distortions, it can be easily recovered upon the discharging process. Therefore, the SE-LCO is able to undergo an more reversible slip of Co-O layers upon high-voltage cycle.

To further unravel the benefit role of the optimized surface chemistry on enhancing the long-term cycle stability of SE-LCO, SEM and TEM

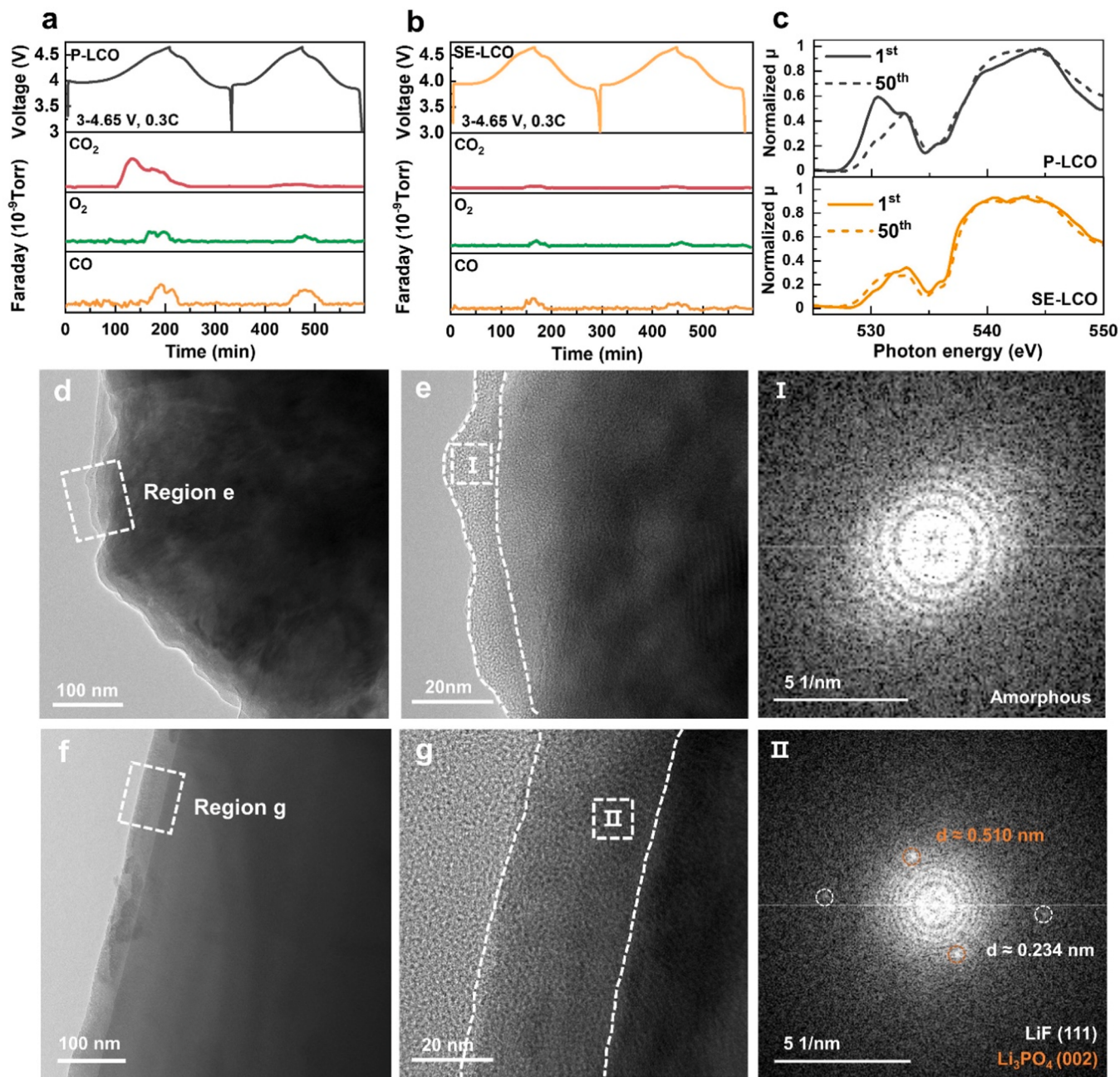


Fig. 6. Side reactions and CEI characterization. (a, b) Comparison of DEMS results of P-LCO and SE-LCO in 3–4.65 V and at current of 0.3 C. (c) Comparison of the soft X-ray absorption spectrum results of P-LCO and SE-LCO. (d, e) TEM characterizations of CEI layers on P-LCO, and correlated diffraction pattern. (f, g) TEM characterizations of CEI layers on SE-LCO, and correlated diffraction pattern.

measurements are further performed. Fig. S19 shows the surface and cross-section morphologies of P-LCO and SE-LCO after 300 cycles (in LCO/Li cells) at 1 C and 4.6 V. For P-LCO, a typical step-like morphology on the surface, and severe cracks across the entire LCO particle are clearly observed. By comparison, the particle integrity of SE-LCO is well maintained without visible cracks, mainly due to the optimized surface chemistry, which guarantees the highly reversible phase transition upon cycles. The detailed structure evolution is further characterized by TEM, especially in the near-surface regions. As seen in Fig. 5a,c, after 300 cycles, a badly damaged surface containing a large number of micro-cracks and micro-holes is observed in the surface region of P-LCO, while for SE-LCO, the high surface integrity can be retained. Fig. 5b, d further show the surface structure upon more subtle observation scales. For P-LCO, the surface structure has completely transformed to

spinel phase, and the spinel/layer hybrid structure can be detected even in a high depth of 50 nm (from surface), indicating the severe structure collapse in the surface of P-LCO. As for SE-LCO, it still retains the pristine surface structure, with surface RS layer, subsurface spinel-like layer, as well as layered structure in the bulk, demonstrating the beneficial effect of the optimized surface chemistry on stabilizing the surface structure. Therefore, optimizing surface chemistry can avoid the step-like surface degradation, and can significantly enhance the structure stability of both the surface and bulk regions of SE-LCO upon long-term cycles.

2.4. Reduced side reactions

As described above, the generation of step-like degradation in the surface of P-LCO leads to the exposure of more plane edges as active

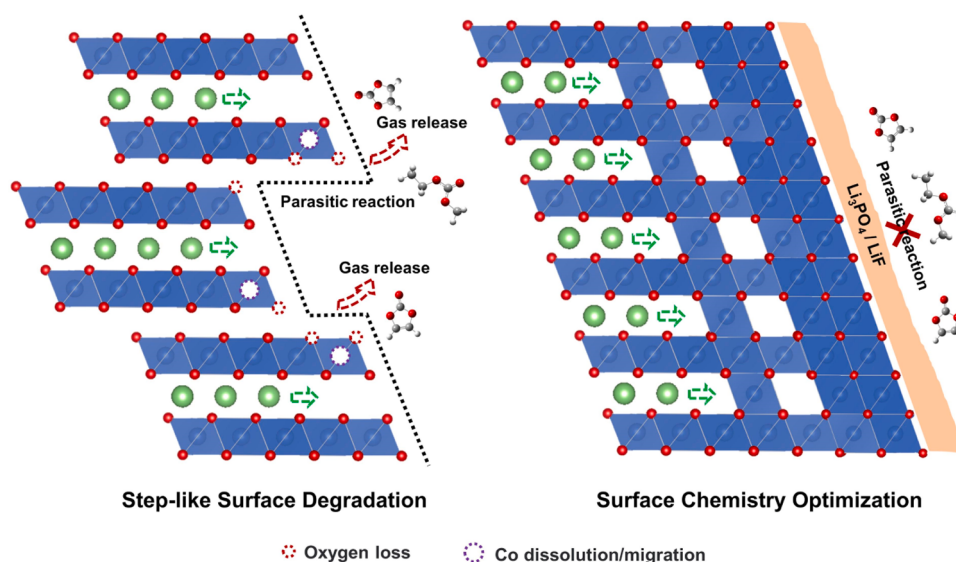


Fig. 7. Schematic illustration of the beneficial role of surface chemistry optimization on reducing the step-like surface degradation of high-voltage LCO at 4.6 V.

catalytic sites, which can increase the risk of lattice O loss and side reactions [38–40]. In order to illustrate the essential role of the optimized surface chemistry on suppressing the lattice O loss from surface region of SE-LCO, the differential electrochemical mass spectroscopy (DEMS) tests are utilized in initial two cycles in a potential range of 3–4.65 V (in LCO/Li cells), as shown in Fig. 6a,b. The release of O_2 operating at high voltage can be obviously observed for P-LCO, while it significantly decreases for SE-LCO, indicating lesser O_2 release from surface. Besides, the release of CO_2 and CO is also successfully inhibited in SE-LCO/Li cell, indicating the lesser decomposition of carbonate solvents in electrolyte.

To further characterize the lattice O loss upon cycles, the O K-edge of soft X-ray absorption spectrum (sXAS) is further performed under the surface-sensitive total electron yield (TEY) mode (Fig. 6c,d). The relative ratio of the pre-edge peak (about 532 eV) and main peak (about 535–550 eV) can semi-qualitatively examine the O loss degree in two kinds of LCO cathodes [41]. After cycles, the pre-edge peak intensity of P-LCO reduces significantly due to the serious lattice oxygen loss from the surface, while for SE-LCO, the pre-edge peak intensity reduces slightly, revealing that the lattice O loss can be effectively suppressed upon cycle due to the more stabilized surface oxygen framework. The combined results of DEMS and sXAS demonstrate that the O loss and side reactions can be suppressed due to the optimized surface chemistry of SE-LCO. Benefited from the stabilized O framework of SE-LCO, the Co dissolution from the surface is also inhibited upon cycles, as confirmed by the Co 2p spectra results in Fig. S20.

At high voltage, the O loss from surface of LCO can cause the interface chemical reactions between the released O_2 and organic solvents, thus leading to the formation of unsatisfactory CEI [42]. TEM is further carried out to characterize the CEI morphology and existence state on surface of the cycled P-LCO and SE-LCO. As shown in Fig. 6e,f, the CEI layer on surface of P-LCO shows a thin and uneven feature, while for SE-LCO, the CEI is quite uniform and compact. Upon more subtle observation (Fig. 6g,h), the thickness of CEI on surface of cycled P-LCO is less than 10 nm, and displays a nearly amorphous state. For cycled SE-LCO, the CEI presents different feature, with a thickness of nearly 40 nm, and is homogeneously and compactly attached on the surface of SE-LCO. Besides, by analyzing the diffraction patterns, the diffraction spots representing the (111) plane of LiF phase (white arrows) and (002) plane of Li_3PO_4 (orange arrows) are observed in CEI of cycled SE-LCO, which is totally different from the CEI of cycled P-LCO.

In addition, in-depth XPS measurements are applied to probe the detailed CEI compositions on surface of two cycled LCO cathodes

(Fig. S21). It can be observed that, there are three kinds of F species in CEI, including the LiF, $Li_xPF_yO_z$ and PVDF [30,43,44]. The content of LiF in surface of cycled SE-LCO is obviously higher than of P-LCO, indicating the higher protectiveness of CEI [45]. Besides, we further observe that, the peaks of Li_2CO_3 (about 291.0 eV) and $O-C=O$ (about 287.9 eV) of SE-LCO are significantly lower than that of P-LCO, demonstrating that the decomposition of carbonate solvents is substantially suppressed on surface of SE-LCO, corresponding to the DEMS results in Fig. 6a,b. In summary, a stable LiF-rich CEI is constructed on surface of cycled SE-LCO, mainly attributing to the optimized surface chemistry, which helps to stabilize the surface stability of SE-LCO.

As described above, optimizing surface chemistry of SE-LCO brings the dual stabilization of surface CEI and surface structure, which is responsible for the enhanced cycle stability. To probe the beneficial effects of the optimized surface chemistry, electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT) measurements are applied to analyze the interface evolution of P-LCO and SE-LCO. As shown in Fig. S22, the EIS plots of two kinds of LCO/Li cells after 50th, 100th, and 200th cycles are plotted and fitted. The obtained R_{sf} value represents the property of CEI layer, and the obtained charge transfer resistance (R_{ct}) value represents the property of surface structure [43,44,46]. 1st, the R_{sf} value of SE-LCO is obviously lower than P-LCO upon cycles, which agrees well with the more stable and uniform LiF-rich CEI film. 2nd, SE-LCO exhibits much smaller and more stable R_{ct} value upon cycles, suggesting that the optimized surface chemistry can effectively avoid the rapid collapse of near-surface structures. Attributing to the dual stabilization of CEI layer and surface structure, the cycled SE-LCO shows much higher diffusion kinetics than that of P-LCO, as confirmed by the galvanostatic intermittent titration technique (GITT) results in Fig. S23.

Combining the results above, the optimization mechanism of tuning surface chemistry to reduce the step-like surface degradation of LCO at 4.6 V is illustrated in Fig. 7. For P-LCO with pure layered structure in both the surface and bulk, some Co-O layer will experience severe slippage due to the over-delithiation, leading to the generation of step-like surface degradation. This kind of surface degradation leads to the exposure of more fresh layer edges, acting as the active catalytic sites to promote the electrolyte decomposition on the LCO surface, leading to severe O loss, side reactions, and irreversible phase transition, which is responsible for the rapid capacity decay. While for SE-LCO with optimized surface chemistry, the above issues are efficiently prevented. The optimized surface chemistry enables an enhanced but more reversible phase transitions of SE-LCO, and promotes the formation of tough CEI

layer to suppress the O loss and Co dissolution issues. As a result, both the cycle and rate performances of SE-LCO is significantly enhanced.

3. Conclusions

In summary, this work reveals a novel step-like surface degradation for high voltage operation of P-LCO, and provides a high-performance LCO cathode with a optimized surface chemistry (SE-LCO). The cycle and rate performances of SE-LCO is significantly enhanced due to the optimization of surface chemistry. Especially, the SE-LCO/graphite cell achieves excellent cycle stability with a remarkable capacity retention of 81.2% after 800 cycles in 3–4.55 V, which is among the best reported cell performances. The benefiting effects is attributed to not only the stabilized surface structure, featuring the outermost surface Li_3PO_4 , surface rock-salt layer, and subsurface spinel-like layer, but also the formation of tough CEI layer closely relating to the optimized surface chemistry. Our work provides useful guidance on surface designs of the advanced cathode materials for LIBs.

CRedit authorship contribution statement

Zirui Lou: Project administration, Methodology. **Jiajie Liu:** Resources, Methodology. **Haocong Yi:** Data curation. **Haocheng Ji:** Data curation. **Hengyu Ren:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Qinghe Zhao:** Writing – review & editing, Visualization, Resources, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Xiaohu Wang:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Feng Pan:** Visualization, Project administration, Methodology, Conceptualization. **Lin Zhou:** Funding acquisition. **Wenguang Zhao:** Resources, Data curation. **Qingrui Pan:** Data curation, Resources. **Zijian Li:** Formal analysis, Data curation. **Yuhao Du:** Investigation, Formal analysis, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.nanoen.2024.109537](https://doi.org/10.1016/j.nanoen.2024.109537).

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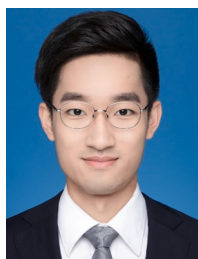
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