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Misfit strain-induced mechanical cracking aggravating surface degradation of LiCoO_2

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ABSTRACT

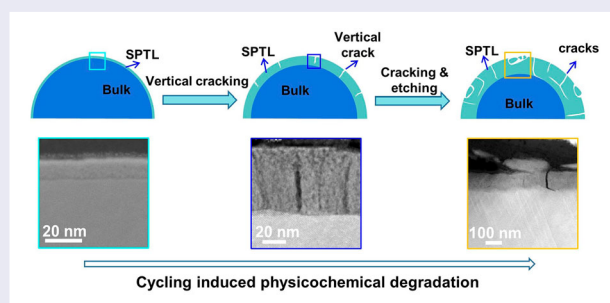
Cycling-induced cathode interfacial degradations are usually attributed to chemical process, while the physical effect is overlooked to a large extent. Herein, we investigate the failure mechanism of LiCoO_2 cathode and reveal that misfit strain plays a dominant role in the surface layer exfoliation process. We illustrate that highly strained LiCoO_2 surface can initiate massive surface cracks, leading to the LiCoO_2 surface layer broken and exfoliation. Mechanical cracking coupled with chemical etching aggravates the surface layer degradation, leading to a weathering-like degradation on LiCoO_2 surface. Our work reveals that interfacial degradation of electrode materials is a complex physicochemical process.

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Lithium-ion battery; LiCoO_2 ; misfit strain; cracking; electron microscopy



Impact Statement

Interfacial degradations are usually believed as chemical effect dominated failure. Herein, we show that the overlooked physical effect, misfit strain, in fact plays a critical role in the surface degradation process and stress that LiCoO_2 surface degradation is a complex physicochemical process.

1. Introduction

Solid/liquid interfaces in a rechargeable battery govern the charge transfer kinetics thus playing key roles in determining battery performance [1–4]. Chemical instability-induced interfacial degradations at the cathode side is particularly important, which mainly include cathode/electrolyte interphase (CEI) formation [5,6], surface layer phase transformation [7–9], reduction and

dissolution of transition metal ions [10,11] and oxygen loss [12–14]. CEI passivation layer and surface phase transformation layer (SPTL) are acting as blocking layers for charge transfer, causing voltage fading, capacity decay and poor rate capability [5,7]. Cathode surface erosion and fragmentation is a typical interfacial degradation, which causes the dissolution of transition metal (TM) ions into electrolytes [15,16]. TM migration and

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dissolution can accelerate irreversible structural transformation of cathode and passivate active surface, blocking lithium-ion intercalation and deintercalation [11,17]. TM loss also can induce surface pits, voids and cracks, which have been frequently observed at the layered cathode surface after electrochemical cycling [18,19]. These defects expose inner bulk to electrolyte, causing new sites for interfacial degradation [20]. Continuously interfacial side reactions not only consume electrolyte but also cause gradual capacity decay due to the loss of active cathode materials [15]. Moreover, the dissolved TM cations not only catalyze the decomposition of the electrolyte but also migrate and deposit on electrode surface causing SEI layer instability [17,21]. Fully understanding the cathode interfacial degradation is vital for realizing high cycling performance.

The chemical effect on cathode surface degradation has been widely recognized, such as surface etching, surface side reactions, especially the attack of acid HF species [16,22,23]. Electrochemical cycling of layered structure can also lead to mechanical degradations, which is mainly due to delithiation-induced lattice deformation and phase transition [24–27]. Such a physical effect incurs increasing attention recently and has been investigated intensively [28]. As for the surface degradation layer, the lattice misfit strain between the surface phase transition layer (SPTL) and the matrix can cause an innegligible issue, which has not been studied systematically. In this work, we take commercial LiCoO_2 cathode as an example to reveal the interfacial degradations and its evolution process upon prolonged cycles. Through microscopic characterizations and theoretical simulations, we show that LiCoO_2 particles undergo a weathering-like surface degradation, in which misfit strain-induced mechanical cracking plays a key role in facilitating the SPTL exfoliation process. Our work highlights that mechanical failure plays an important role in the interfacial degradation process for those electrode materials suffering high interfacial strain.

2. Experimental section

2.1. Electrochemical performance tests

LiCoO_2 cathode materials were purchased from Shenzhen Kejing Star Technology Co. Ltd. The electrochemical performance was tested with 2032 coin-type cells. First, the cathode electrodes, carbon black and polyvinylidene difluoride (PDVF) are mixed at a weight ratio of 8:1:1 in NMP stirred for 6 h. Then, slurry was cast onto carbon-coated Al foil current collector.

The carbon-coated Al foil with slurry is dried in a vacuum oven for 12 h at 60°C. All coin cells are assembled in an argon-filled glovebox with a metallic lithium foil

as the counter electrodes, a Celgard 3501 polypropylene membrane as a separator, and the 1 M LiPF_6 in ethylene carbonate and ethyl methyl carbonate (3:7 EC:EMC weight ratio) as the electrolyte. All cells are cycled at 0.2C rate (1C = 140 mA/g) with different voltage windows, 2.7–4.4 V, 2.7–4.55 V and 2.7–4.7 V.

2.2. Characterization methods

SEM imaging and TEM specimen preparation were conducted on an FEI Helios DualBeam Focused Ion Beam operating at 2–30 kV. First, a 1- μm -thick Pt layer was deposited on a region to avoid Ga ion beam damage in the subsequent lift-out and thinning process. After lift out, the specimen was thinned to 200 nm using 30 kV Ga ion beam by reducing the current gradually. Then the surface was polished by a 5-kV Ga ion beam to remove the surface damage layer and further thinning to electron transparency. Finally, a 2-kV Ga ion beam was used to clear the surface damage layer. Specimens were characterized using a probe spherical aberration transmission electron microscope (FEI Titan G2 60-300) with an acceleration voltage of 300 kV. In-situ X-ray diffraction (XRD) tests were carried out using a Bruker D8 Advance X-ray diffractometer.

3. Results and discussion

3.1. Interfacial degradations dominating LiCoO_2 decay at 4.2 V

When cycled at voltage window 2.7–4.2 V, LiCoO_2 performance decay is mainly due to the incremental capacity loss, while the voltage fading is negligible. As shown in Figure 1(a), the capacity retention is 83% after 500 cycles. Figure 1(b) shows the voltage fading is negligible. To understand the origins of LiCoO_2 capacity decay, the cycled electrode is characterized by electron microscopy and XRD. Our results indicate that grain bulk does not show any appreciable changes even after 500 cycles at 2.7–4.2 V (Figure 1c, d and Figure S1). As revealed by the selected area electron diffraction (SAED) pattern (Figure 1c) and high angle annular dark field (HAADF) lattice image (Figure 1d), layered structure is well preserved. In contrast, we observed severe interfacial degradations at LiCoO_2 surface. As shown in Figure 1(c), the surface phase transformation layer (SPTL) is as thick as 110 nm, and massive cracks are generated in the surface layer as denoted by the yellow arrows. More tiny cracks can be seen from the high magnification TEM image in the SPTL as shown in Figure 1(e), indicating the cracks are originated at the LCO/SPTL interface. The lattice structure of SPTL is a spinel-like structure (Figure S2) and many etching dots are formed (Figure 1e) due to

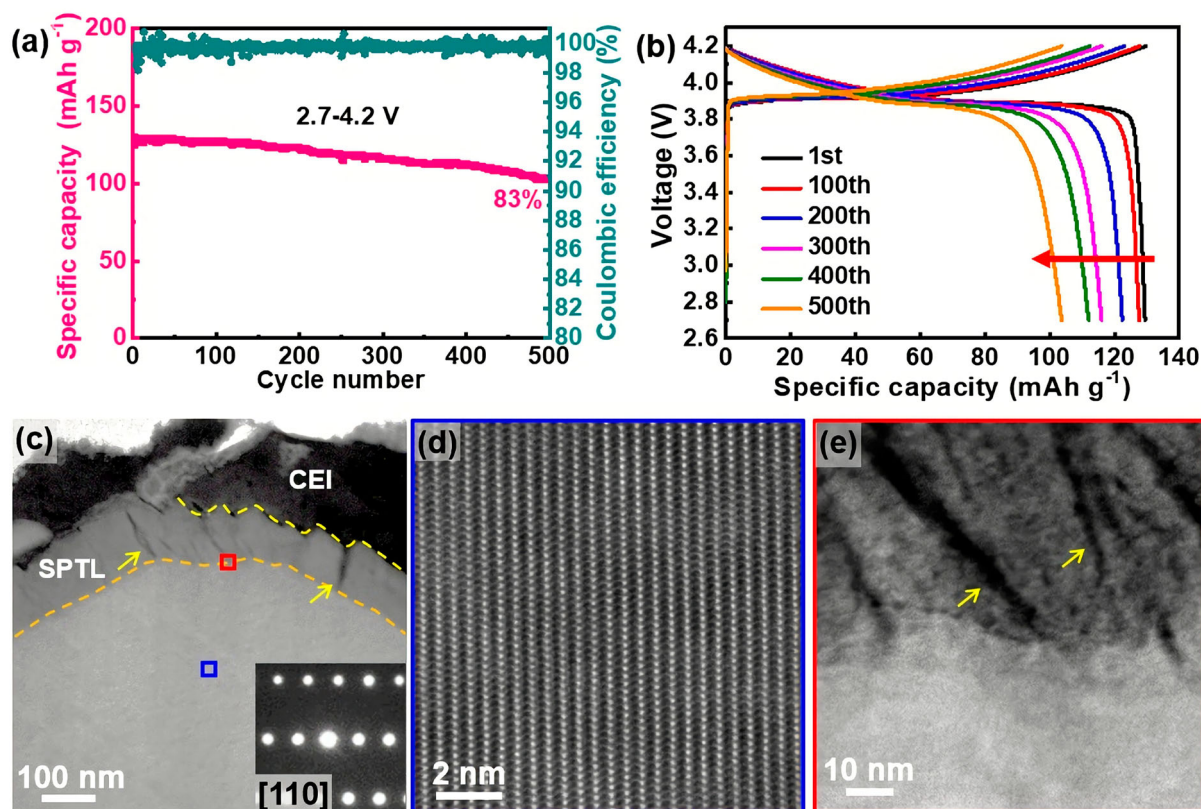


Figure 1. Electrochemical performance and microstructure characterizations. The LCO/Li-metal half-cell is cycled at 0.2 C rate ($1C = 140 \text{ mA g}^{-1}$) in the voltage window 2.7–4.2 V. (a) Capacity retention and corresponding coulombic efficiencies. (b) The corresponding charge/discharge voltage profiles, showing only capacity decay is significant (highlighted by the red arrow). (c) STEM-HAADF image to show a LiCoO_2 particle after 500 cycles. Many cracks are formed in the SPTL highlighted by yellow arrows. Inset diffraction pattern is from the grain bulk, showing the well-preserved layered structure. (d) The lattice image from the blue area in (c), reveals the well-defined layered structure in the bulk. (e) Enlarged image from the red area in (c) to show the defective SPTL with high density of cracks and voids (dark contrast).

massive Co dissolution and O loss as evidenced by EDS mapping (Figure S3). Our characterizations indicate that interfacial degradations are the major cause of the performance decay for the LiCoO_2 cathode cycled at 2.7–4.2 V. Similar results were obtained from the sample after 300 cycles at 2.7–4.2 V (Figure S4).

3.2. Mechanical cracking induced surface layer exfoliation

The SPTL thickness increases with increasing the cycle numbers. As shown in Figure 2(a–c), under 2.7–4.2 V operation, the typical SPTL thickness is about 11 nm after 50 cycles, 45 nm after 100 cycles and 180 nm after 500 cycles. With the increase of the SPTL thickness, surface cracks are gradually developed. The crack density increases with increasing cycle numbers as shown in Figure 2(b–d). The cracks are first initiated from the SPTL (Figure 2b), which are vertical to the SPTL/matrix interfaces, and with the thickness increase of the SPTL, the cracks deflect to the SPTL/matrix interfaces as indicated by red arrows in Figure 2(c, d) and Figure S5.

The vertical cracks and the interfacial cracks are indicated by yellow arrows and red arrows, respectively. As shown in Figure 2(e), further extending the interfacial cracks along the interface finally leads to the SPTL exfoliation. Surface SPTL exfoliation is not homogeneous, which leads to a bumpy surface morphology and the SPTL thickness varies accordingly. More examples are shown in Figure S6. Figure 2(f) illustrates the whole evolution process of the LCO surface during cycling. First, a uniform SPTL layer is formed at the LCO surface and then vertical cracks are developed in the SPTL. Further increasing the SPTL thickness leads to interfacial cracks along the SPTL/matrix interfaces, which causes the exfoliation of the SPTL. Electrolyte penetration into the freshly formed cracks leads to a chemical etching effect, which can significantly accelerate the exfoliation of the SPTL.

3.3. Misfit strain-induced cracking.

When the LiCoO_2 surface undergoes degradation, its original layered structure transforms into the spinel-like

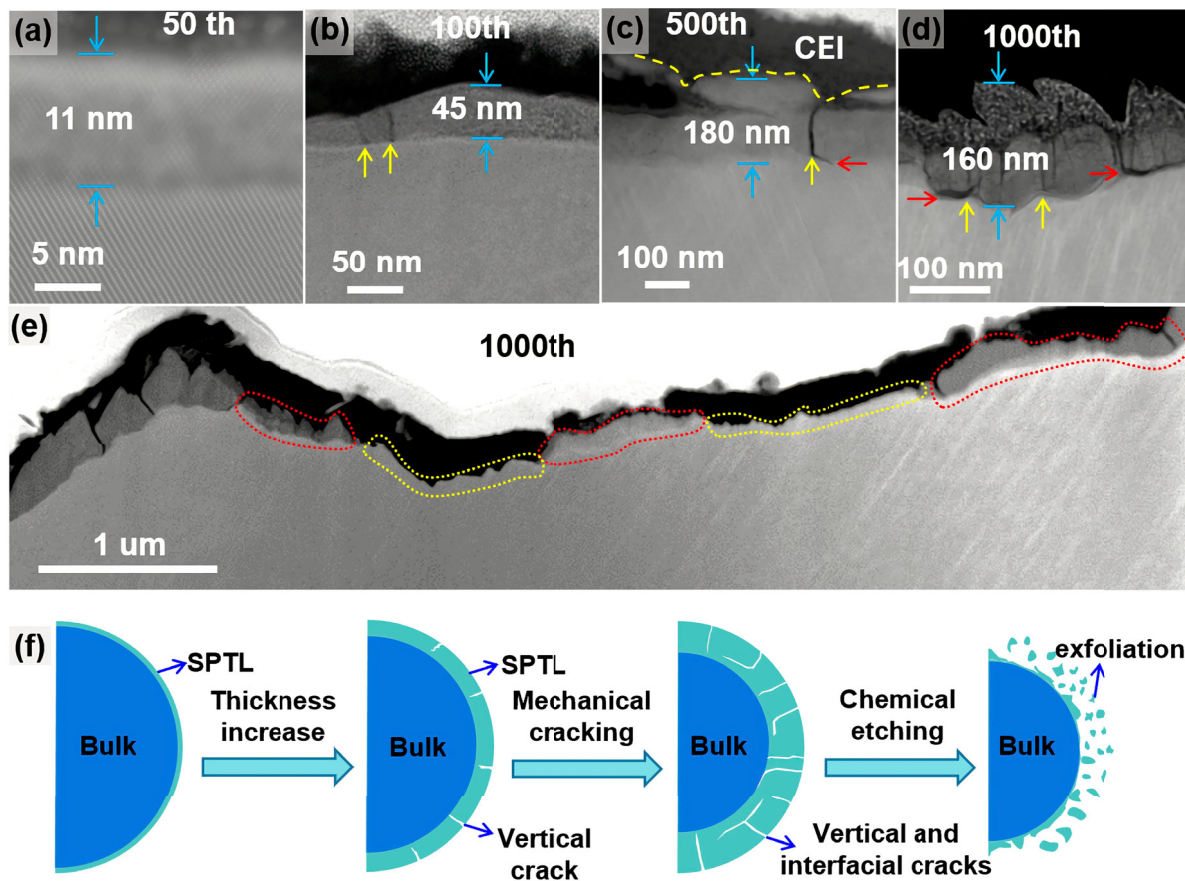


Figure 2. Surface cracking and exfoliation process. (a–c) STEM-HAADF images show the SPTL thickness after different cycle numbers. The vertical cracks (yellow arrows) are formed in (b) after 100 cycles. The interfacial cracks (red arrows) are formed after more cycles in (c, d). (d, e) STEM-HAADF images of LiCoO₂ particle after 1000 cycles, showing the SPTL are exfoliated. The SPTL shows gray contrast on the LCO surface. Completely exfoliated SPTL is highlighted by the dashed yellow lines. (f) Schematic diagrams to illustrate the surface layer exfoliation process during the cycling of LiCoO₂.

structure. As shown in the STEM-HAADF images (Figure 3a–c), the SPTL is epitaxially grown on the LiCoO₂ substrate after 300 cycles, in which the SPTL (111) plane is parallel to the layered (003) planes. As shown in Figure 3(b), the plane spacing of layered (003) is 4.73 Å, while the SPTL (111) plane spacing is 4.67 Å. Although the lattice mismatch is small ($\sim 1.3\%$) between the SPTL and the LiCoO₂ substrate, misfit strain still accumulates upon the SPTL growth. Figure 3(d) illustrates that when the SPTL exceeds a critical thickness (h), crack will be initiated to release the misfit strain energy. Crack relaxes strain energy but gives rise to new surface energy. Only when the relaxed strain energy is greater than the surface energy, cracking becomes energetically favorable [29]. According to the film-substrate system, the critical thickness (h_c) for crack formation is given by

$$h_c = \frac{\Gamma E_{\text{SPTL}}}{Z\sigma^2(1-\nu^2)} \quad (1)$$

where Γ is the fracture resistance which is equal to the SPTL (111) plane surface energy, E_{SPTL} is the Young's

modulus, ν is the Poisson's ratio, Z is a dimensionless driving force, depending on the cracking pattern and elastic mismatch. Generally, thin film cracking models could be classified into five different types: surface crack, channeling, substrate damage, spalling and debonding [30]. In our case, the cathode particle exhibits channeling cracks without bulk damage, as shown in Figure 3(d). Therefore, $Z = 1.976$ [30]. σ is the stress experienced by lattice mismatch at the SPTL/bulk interface, which is characterized as uniaxial tensile stress [31]

$$\sigma = E_{\text{SPTL}} \frac{(d_{\text{bulk}} - d_{\text{SPTL}})}{d_{\text{bulk}}} \quad (2)$$

where d_{bulk} is the (003) plane spacing and d_{SPTL} is the SPTL (111) plane spacing.

The calculation parameters are listed in Table S1 [32,33]. Due to lithiation/delithiation induced lattice breathing, the (003) plane can reach 4.81 Å at 50% delithiation (Li_{0.5}CoO₂), which is evidenced by our in-situ XRD test (Figure S7) and previous result [34]. Thus the critical thickness h_c is estimated as 13 nm, which is consistent

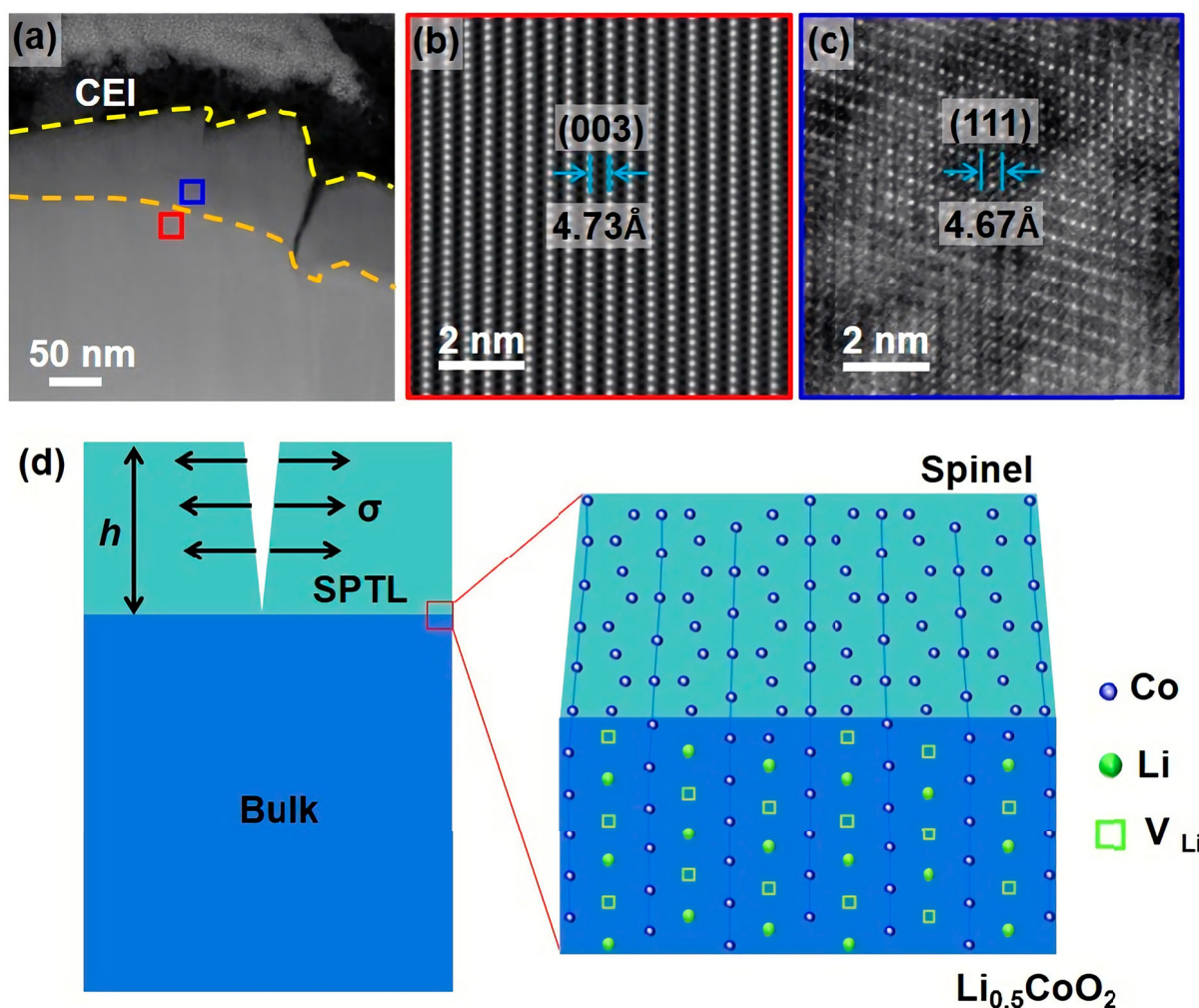


Figure 3. Misfit-strain induced surface crack. (a–c) STEM-HAADF images of a LiCoO_2 particle after 300 cycles. High-resolution lattice images from (b) the LCO substrate and (c) the SPTL, where the plane spacing of layered (003) is 4.73 Å and that of spinel SPTL (111) planes is 4.67 Å. (d) A film-substrate model to show the crack generation in the SPTL under tensile stress. Enlarged interfacial lattice structure model shows the misfit strain between delithiated LCO and SPTL.

with our experimental observations that cracks are usually generated in the SPTL thicker than 20 nm (Figure 2 and Figure S8).

To further investigate the crack propagation for the SPTL beyond the critical thickness, an electrochemo-mechanical phase field model is developed. The anisotropic lithium diffusion, the heterogeneous structure containing an SPTL and LCO matrix, and electrolyte penetration into the propagating surface crack are considered in this model. The detail description is shown in Figure S9. Since the SPTL thickness affects crack formation and crack propagation (Figure 2), 90 nm SPTL (thin model) and 180 nm SPTL (thick model) are considered for the simulation. The crack propagation and stress evolution are shown in Figure S10 and Figure 4 (the enlarged images of the crack region in Figure S10). Misfit strain and lithium gradient-induced strain are considered as shown in Figure S11 and the stress caused by the

SPTL and the lithium gradient are shown in Figure S12 and Figure S13, respectively, which demonstrates that the stress magnitude is mainly determined by the SPTL due to the large lattice mismatch. The simulation results show that the crack grows vertically to the bulk/SPTL interface and stops at the interface for the thin SPTL model (Figure 4a). While for the thick SPTL model, when the surface vertical crack reaches the SPTL/bulk interface, it deflects to the interface (Figure 4b). The reason why the crack can deflect to the SPTL/bulk interface rather than penetrating the LCO matrix is attributed to two main reasons. One is that the stress magnitude caused by the thick SPTL is large enough to trigger the interface crack. The other is that the fracture resistance of LCO is higher than that of the SPTL, which prevents the crack to penetrate the LCO substrate. Our experimental observations also validate that the LCO underneath the SPTL is defect free (as shown in Figure S14). Note

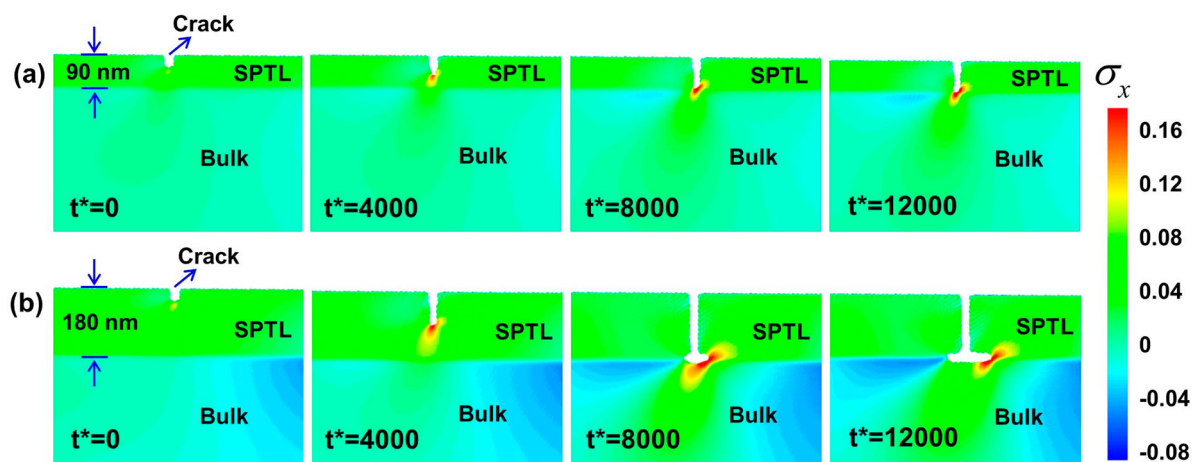


Figure 4. Simulation of the crack propagation. The evolutions of dimensionless hydrostatic stress and the set surface crack at different dimensionless times $t^* = 0, t^* = 4000, t^* = 8000$ and $t^* = 12000$. (a) Thin SPTL model. When the SPTL thickness as 90 nm, the crack propagates vertically to the bulk/SPTL interface. (b) Thick SPTL model. The crack grows vertically and then bent to interfacial at the bulk/SPTL interface.

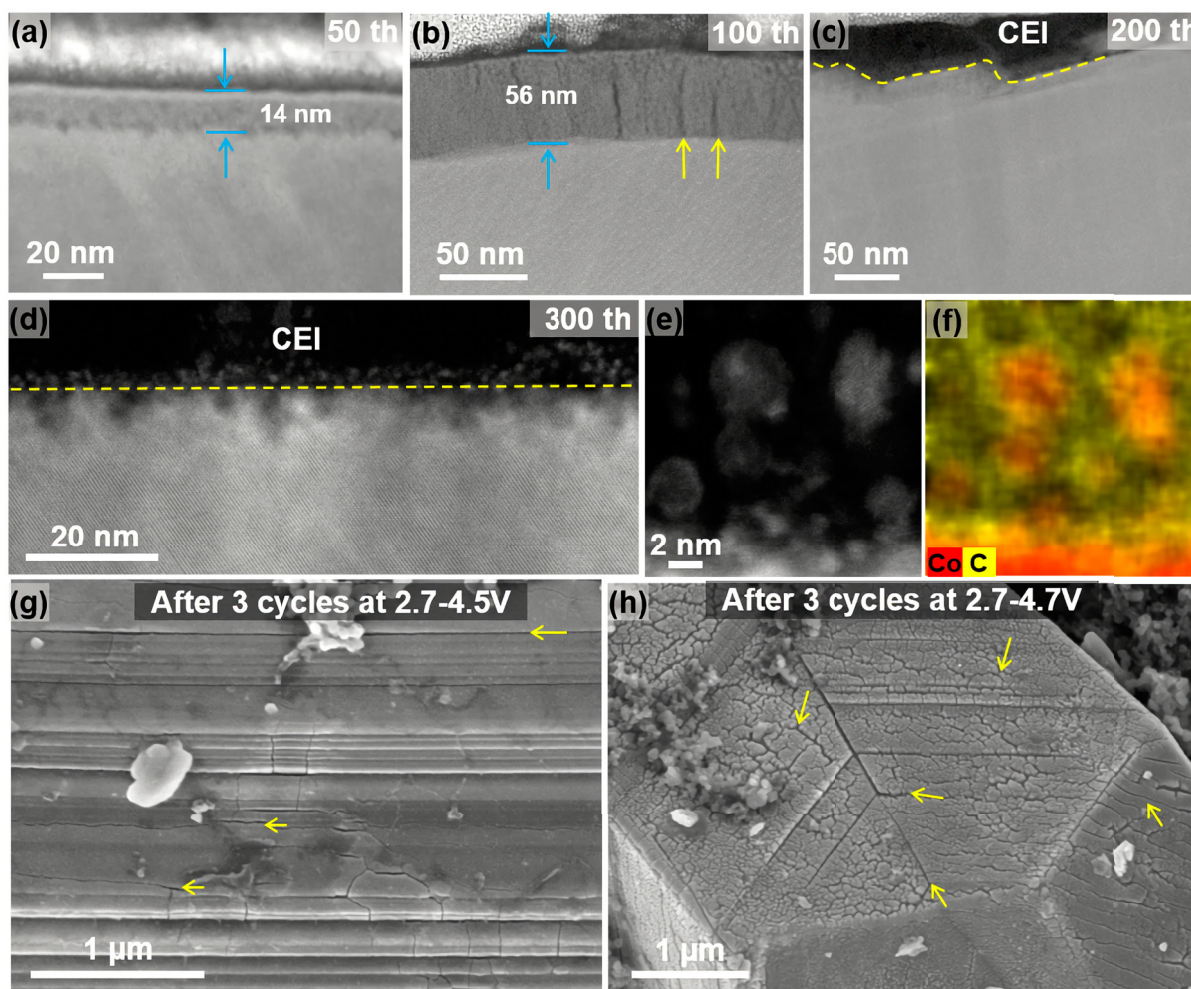


Figure 5. Evolution of the SPTL when cycled at 2.7–4.4 V. (a–d) STEM-HAADF images to show the thickness of the SPTL when cycled at 2.7–4.4 V at different cycle numbers. The SPTL exfoliation is observed in (c, d). (e, f) EDS-mapping images show the fragmented pieces near the surface of bulk including Co elements and strong C signal, indicating that the SPTL fragments are entrapped in the CEI layer. (g–h) SEM images to show the massive cracks formed on the surface of LiCoO₂ particle cycled at higher voltages, 4.5 and 4.7 V respectively.

that deflection cracks into the SPTL/bulk interface causes the SPTL exfoliation from particle surface, which is detrimental.

It is worth mentioning that the interfacial strain can also originate from the CEI layer. As shown in the TEM images, a thick CEI layer is usually found on the top of the SPTL. Based on the previous investigations, Young's modulus of SEI is usually below 5 GPa [35–39], which is much lower than that of the LCO substrate (191 GPa) [40]. Therefore, in our case the CEI-induced strain is negligible. However, if the cathode particle is a secondary particle with the presence of cycling-induced massive cracks, the CEI-induced strain is not negligible anymore [41,42]. Additionally, based on our TEM observations, cracks can nucleate both from the LCO/SPTL interface and the SPTL/CEI interface (as shown in Figure S15), indicating the intricate chemo-mechanical coupling effect in facilitating the crack nucleation.

High voltage LiCoO₂ is attracting increasing attention due to its high energy density. Our observations show that increasing the charge cutoff voltage leads to severe surface degradations. As shown in Figure 5(a–f) and Figure S16, the LCO sample is cycled at 2.7–4.4 V, SPTL exfoliation occurs significantly faster. The faster interfacial degradation leads to faster performance decay. The capacity retention is 59% after 300 cycles at 2.7–4.4 V cycling (Figure S17). The SPTL is observed again with extended cycling (e.g. the sample after 700 cycles) as shown in Figure S18, indicating that the SPTL undergoes formation–exfoliation–reformation process upon continuous cycling. Massive small fragmented pieces are found in the CEI layer as shown in Figure 5(d–f) and Figure S19. Increasing the cutoff voltage to 4.5 and 4.7 V, LCO surface cracks can be observed only after two cycles as shown in Figure 5(g, h).

Cycling-induced surface structure reconstruction is a very common behavior for many battery materials, including other layered cathodes, spinel-structure cathodes, olivine-structure polyanion cathodes and other electrode materials for rechargeable batteries [43–47]. As long as the surface reconstruction layer is developed, the misfit strain builds up. Mechanically, the strain can generate cracks to cause particle fragmentations. Chemically, strain can assist chemical etching and corrosion to speed up the surface degradation process. The degradation is a complexed physicochemical process, which mimics the rock weathering process as illustrated in Figure S20 [48]. Such a crack–corrosion–exfoliation process is more than a pure chemical etching effect. Therefore, to effectively stabilize the interface/surface of battery materials, it is essential to consider both physical and chemical effects together.

4. Conclusion

Through intensive microscopy analysis of the surface degradation process of LiCoO₂, we reveal that the misfit-strain induced cracking plays a critical role in the surface degradation process. Such physical effect initiates cracks and fresh surfaces, which exaggerates the chemical effects, like side reactions, etching and corrosion. Combining the physical and chemical effects, the LiCoO₂ surface suffers a weathering-like surface degradation process, featuring with surface layer exfoliation and corrosion. Surface degradation-induced surface structure reconstruction is a common phenomenon for various battery materials. Our work stresses that physical strain effect can be a dominant factor for surface layer degradation, which further deepens our understanding of the interfacial degradation mechanisms of battery materials and provides valuable insights for stabilizing interface/surface.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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