Dynamic behaviour of interphases and its implication on high-energy-density cathode materials in lithium-ion batteries

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Undesired electrode-electrolyte interactions prevent the use of many high-energy-density cathode materials in practical lithium-ion batteries. Efforts to address their limited service life have predominantly focused on the active electrode materials and electrolytes. Here an advanced three-dimensional chemical and imaging analysis on a model material, the nickel-rich layered lithium transition-metal oxide, reveals the dynamic behaviour of cathode interphases driven by conductive carbon additives (carbon black) in a common nonaqueous electrolyte. Region-of-interest sensitive secondary-ion mass spectrometry shows that a cathode-electrolyte interphase, initially formed on carbon black with no electrochemical bias applied, readily passivates the cathode particles through mutual exchange of surface species. By tuning the interphase thickness, we demonstrate its robustness in suppressing the deterioration of the electrode/electrolyte interface during high-voltage cell operation. Our results provide insights on the formation and evolution of cathode interphases, facilitating development of in situ surface protection on high-energy-density cathode materials in lithium-based batteries.
Considerable interest has been directed towards the development of reliable, low-cost, high-energy-density rechargeable Li-ion batteries to meet the demands of multiple emerging fields, such as advanced robotics, electric vehicles and grid storage. This has motivated extensive investigation of cathode materials with higher operating voltages than conventional LiCoO$_2$ (upper cutoff voltage of ~4.2 V vs Li/Li$^+$) to maximize energy-storage capabilities. Potential candidates include Ni-rich layered oxides $^{6-8}$ (LiNi$_{1-x}$M$_x$O$_2$ with M = metal ~4.5 V), Li-rich layered oxides $^{9-11}$ (Li$_{1+x}$M$_{1-x}$O$_2$ with ~4.7 V), high-voltage spinel oxides $^{12,13}$ (LiNi$_{0.5}$Mn$_{0.5}$O$_2$ with ~4.8 V) and high-voltage polyvalent compounds $^{14-16}$ (phosphates and sulfates, up to ~5.2 V). Unfortunately, these cathodes suffer from limited service life due to aggressive electrochemical degradation initiated at the electrode–electrolyte interface. This is largely caused by their operating voltages extending over the electrochemical stability window of most known nonaqueous electrolytes in lithium-ion batteries. $^{2,4,5,17}$ For instance, commercial ethylene carbonate (EC)-based electrolytes with lithium hexafluorophosphate (LiPF$_6$) as the salt have a stability window of ~1.3–4.3 V vs Li/Li$^+$. Moreover, oxidative decomposition of electrolyte components at high-voltage operation is not the only concern; often, surface degradation on cathodes involves active mass dissolution (for example, Mn$^{2+}$) $^{18-20}$ and irreversible structural reconstruction (for example, cation migration) at highly delithiated states. $^{10,11,19,21-23}$

As the quest for alternative, non-reacting electrolyte combinations is a formidable task, most efforts tackling the unsatisfactory cycle life of these high-voltage cathodes attempt to enhance the electrode–electrolyte interface stability with the formation of a stable, robust passivation film, similar to the solid-electrolyte interphase formed on graphite. $^{2,4,17,24}$ This is achieved ex situ by coating or doping of active cathode particles $^{25-27}$, or in situ by employing electrolyte additives. $^{28,29}$ Despite some modest success, effective passivation of the cathode material surface (up to ~5 V vs Li/Li$^+$) remains challenging in the battery community. $^{2,4,5}$ The understanding of interphases formed on cathode materials in existing cell configurations is rather limited as well, in part due to complex influences of the ‘inactive’ conductive carbon additives (for example, carbon black) in composite electrodes, which have not been recognized until recently. $^{14,17,26,30-32}$ This is not surprising since commonly used surface-sensitive diagnostic tools, such as X-ray and infrared spectroscopies, cannot spatially separate different components in electrodes. Undoubtedly, studies on the dynamic formation and evolution of interphases (both spontaneous and under electrochemical cycling) involving the active material and carbon altogether are of pivotal importance and should provide insights on the disputable effects of cathode interphases. $^{4,5,14,18,23-35}$ on electrochemical properties and for further optimization.

Here we use time-of-flight secondary-ion mass spectrometry (TOF-SIMS) to investigate the electrode–electrolyte interphases and their impacts on overall cell performance on a Ni-rich layered oxide cathode (LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$), with a particular focus on the role of conductive carbon. TOF-SIMS offers sub-nanometer surface sensitivity and ultra-high chemical selectivity, and more importantly, region-of-interest (ROI) analysis can be applied to the composite electrode, enabling individual components to be observed independently. $^{36}$ Our results reveal the dominant influence of carbon on the surface chemistry of composite cathode electrodes in common nonaqueous electrolytes. The carbon-driven interphase formed in situ on LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ before cell operation serves as a passivating film against deleterious interfacial reactions with the electrolyte.

**Results**

**Visualization of interphases on cycled LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$:** Figure 1a,b illustrate, respectively, the TOF-SIMS spectra and depth profiles of secondary ions of interest on LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ electrodes during high-voltage electrochemical operation. In Fig. 1a, we witness rapid generation and subsequent marginal, prolonged buildup of organic interphasial species (represented by C$_2$H$_5$O$^-$), together with continuous accumulation of inorganic species during cycling (LiF$^-$); the depth profiles in Fig. 1b, on the other hand, reveal the complex multi-layer characteristics of the interphases on LiNi$_{1-x}$M$_x$O$_2$ particles. Both findings here are consistent with literature results$^{5,13,17,18,33}$, where overall thickening of cathode interphases during cycling is often observed. $^{14,34,37}$ It has been noted that degradation products, including LiF and many organic species, appear localized at the very surface of the interphases (the outer layer), while transition-metal fluorides show high concentrations in the inner layer (where LiF is also abundant). These two ‘layers’ correspond to multiple processes of interfacial dissolution of LiNi$_{1-x}$M$_x$O$_2$ in common LiPF$_6$/EC-based solutions: (i) deposition of salt and solvent (oxidative) decomposition products from the electrolyte $^{4,5,18,33,35}$ and (ii) active mass dissolution aggravated by acidic species attack$^{5,18,25,33}$ (for example, HF—generated in the presence of trace electrolyte impurities, such as H$_2$O). Of particular note, another essential process, the intrinsic structural reconstruction from the layered to the ‘rock-salt’ phase (NiO), also occurs when destabilized transition-metal ions migrate towards neighbouring vacant Li sites at highly delithiated states. $^{19,21,22}$

Illustrative TOF-SIMS chemical mappings were collected on LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ composite electrodes after cycling (Fig. 1c). These maps show that the surface of active cathode particles (represented by the $^{58}$NiO$^-$ fragment), initially covered entirely by degradation-induced chemical species (represented by F$^-$), emerges upon Cs$^+$ sputtering. Detailed visualization in three dimensions of the chemical alterations occurring on the same sample is shown in Fig. 1d,e, and Supplementary Figs 2–4. Additional mappings on the pristine electrodes can be found in Supplementary Fig. 5. The typical surface degradation products in the outer and inner interphases $^{4,5,18,33,35}$ are evidenced by cumulative signals of C$_2$F$^-$, LiF$^-$ and MnF$_2$$^-$ in the top view before and after intensive Cs$^+$ etching in Fig. 1d, as well as in the cross-sectional view with shallow Cs$^+$ milling in Fig. 1e. These degradation products appear mostly located at the surface of secondary particles, although electrolyte penetration along with further attack through micro-cracks towards their interior is possible. $^{6,38,39}$ Notably, transition-metal species ($^{58}$NiO$^-$ and MnF$_2$$^-$) are found on the carbon black/binder surface. It has been shown that the dissolution products from cathode particles eventually make their ways to the graphite anode surface while migrating within the electrolyte during cell operation. $^{4,7,12,13,34}$ A schematic diagram of the complex electrode-electrolyte interfacial chemical and structural evolution during battery operation is depicted in Fig. 1f, with further details in Supplementary Table 2.

**Spontaneous interphase formation on composite cathode electrodes:** Motivated by some recent studies$^{12,14,26,30-32}$ reporting the dominating influence of additive conductive carbon (carbon black) on the behaviour of cathode interphases, we carried out TOF-SIMS measurements aided by ROI selection on aged LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ composite electrodes in LiPF$_6$/EC-DEC. Figure 2a demonstrates TOF-SIMS chemical mapping of two secondary ion fragments, $^{58}$NiO$^-$ (upper) and C$_2$H$_5$O$^-$ (lower), at the electrode surface, representative of active cathode
particles and carbon black/binder, respectively. Two ROIs (ROI-1 and ROI-2) are used accordingly to extract the spectra in Fig. 2bc. Clearly, the ROI selections are highly efficient in spatially separating the fragments of interest, $^{60}$Ni$^-$ (ROI-1) and Cs$^+$ (ROI-2), as seen in Fig. 2b. In Fig. 2c, a series of TOF-SIMS spectra of C$_2$F$^-$, C$_3$OF$^-$, $^7$LiF$_2^-$ and MnF$_3^-$, were retrieved from pristine and aged electrodes for 30 days with different amounts of carbon black (1 and 10 wt.%). Readily obvious is the increase of all four species after aging in both ROI-1 and ROI-2, indicative of ongoing electrode–electrolyte interactions before any acidic species scavenger for the 10 wt.% carbon electrode. The surface species responsible for the C$_2$F$^-$ and C$_3$OF$^-$ fragments observed here originate primarily from two processes: (i) direct acidic species attack (HF) at the surface of carbon black, where dangling bonds of carbon and surface chemical functional groups (such as hydroxyl and carbonyl groups) are abundant and particularly susceptible to acid leaching from the electrolyte with the involvement of carbon black during interphases formation. Further evidence is needed, however, since carbon black, with a much larger relative surface area compared with LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$, serves as an effective acidic species scavenger for the 10 wt.% carbon electrode. 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C₃OF⁻ in good agreement can be found in Supplementary Fig. 7. These findings strongly support that the spontaneously produced surface deposits during aging, such as fluorinated alkane and carbonate species, are mainly a result of acidic species attack on carbon and actively migrate to the cathode particles surface once formed. The resulting surface layer is hereafter referred to as a cathode-electrolyte interphase (CEI), which further evolves upon reactions between carbon black and LiPF₆/EC-DEC. Chemical mapping provides further support of such migration (Fig. 2d), with the cathode particles of 10 wt.% carbon black vividly covered by C₂F⁻ species; whereas for the 1 wt.% electrode, the coverage is less complete. Considering the well-known migration of dissolution products from cathode particles shown above, there exists a dynamic ‘communication’ between the active cathode material and conductive carbon additives during the spontaneous interphases formation in Li-ion batteries, which should have a profound impact on the electrochemical properties.

Tuning the thickness of spontaneously formed CEI. To verify the passivation effects of CEI during high-voltage electrochemical reactions, we prepared three LiNi₀.⁷Co₀.¹₅Mn₀.¹₅O₂ samples with the same bulk chemical composition but different secondary particle sizes (Fig. 3a and Supplementary Fig. 8) through a transition-metal co-precipitation process⁴₈,⁴₀. This enables the direct modification of the CEI thickness, as the active material that has smaller relative surface area (larger particles, Supplementary Table 1) undergoes more in situ spontaneous deposition of surface species from carbon, as demonstrated in Fig. 3b. Powder X-ray diffraction (XRD) confirmed that all as-synthesized samples have a well-defined R₃m layered structure with the cation mixing of around 3%, that is, the content of Ni ions in the Li layer (Supplementary Fig. 9)¹⁹,²²,⁴¹.
The electrochemical performance of LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2 materials in lithium half cells was recorded at room temperature. Figure 3c exhibits typical charge-discharge profiles of LiNi_{0.7}Mn_{0.15}O_2 with a cutoff voltage of 4.5 V vs Li/Li^+ (12-14 μm particle size shown; 8–10 and 18–20 μm particle size in Supplementary Fig. 11). In Fig. 3d-f, the three samples demonstrate different Coulombic efficiencies, hysteresis and capacity fades as cycling proceeds; the sample with larger particles shows better cycling stability. As seen in secondary electron microscopy images of cycled electrodes in Supplementary Figs 12–14, the majority of LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2 particles do not yet exhibit major mechanical fracture at such an early cycling stage (100 cycles) in contrast to many anodes, as their volume change during Li de-intercalation is small (~5%). XRD on cycled electrodes (Supplementary Fig. 15) indicates a marginal increase in cation mixing while all samples retained a good overall layered structure with no apparent bulk phase transformation. Hence, the performance decline is primarily caused by rapid degradation of the electrode/electrolyte interface that induces large over-potentials during charge-discharge processes, which is crucially related to the passivation effect of CEI.

Impedance spectroscopy was, therefore, employed to offer insight to the interfacial evolution for the three samples during cycling. Through this technique, the complex resistance or impedance of all components in an electrochemical cell can be determined. Impedance spectra of LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2/Li half cells at different cycles are given in Fig. 3g,h, and in Supplementary Fig. 16. As a rule, the lower intercept at very high frequency is determined. Impedance spectra of LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2/Li discharged composite electrodes of different particle sizes upon cycling (to 3.0 V vs Li/Li^+) (g) 20 cycles, and (h) 100 cycles. The inset shows the magnified semicircle at the high-frequency region in corresponding main figures. After refreshing with a new Li metal anode and electrolyte after 50 cycles, the cell performance and impedance (Supplementary Fig. 17) do not show improvement, confirming the deterioration of the cathode–electrolyte interface being the main reason for the sluggish charge-transfer kinetic properties; meanwhile, a Bode plot of three discharged electrodes after 100 cycles in Supplementary Fig. 18 indicates the interphases on Li anodes contribute to the first high-frequency semicircle.

Figure 3 | Morphology and electrochemical characterizations of LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2. (a) SEM image of the as-prepared LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2 powder of 12-14 μm in size. Samples prepared through the same method with different secondary particle sizes (8–10 and 18–20 μm) are shown in Supplementary Fig. 8. The specific surface area of the three samples was determined to be, respectively, 0.60, 0.53, and 0.46 m² g⁻¹ via the Brunauer-Emmett-Teller method (Supplementary Table 1). Scale bar, 20 μm. (b) TOF-SIMS spectra of several CEI species (ROI-1 applied and normalized by ROI coverage; integrated over 1,000 s of Cs⁺ sputtering, 10 s interval, two scans per step) on aged LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2 particles after 7 days. Additional spectra of C₂H₂O⁻, C₃H₂O⁻, LiF²⁻, C₂O₃F⁻, C₂OF⁻, MnF³⁻, 58NiF₃⁻, and CoF₃⁻ can be found in Supplementary Fig. 10; the protection of CEI on the active material against acid leaching is readily noticeable among the three samples. (c-f) Galvanostatic charge-discharge tests of three LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2 electrodes of different particle size at room temperature. (c) The evolution of charge-discharge profiles during 100 cycles at C/5 for the 12-14 μm sample. (d-f) Comparison of their Coulombic efficiency, normalized (to maximum) cycling stability and hysteresis (defined here as the difference between average charge and discharge voltages) as cycling proceeds. 1C is equal to 180 mA g⁻¹. The electrochemical profiles of LiNi_{0.7}Mn_{0.15}O_2 materials are characterized by a gradually sloping line with no indication of irreversible oxygen release or bulk layered-to-spinel-like phase transition, commonly seen for Li-rich layered LiNi_{0.7}Mn_{0.15}O_2 (refs 9,10). (g,h) Nyquist plots showing the impedance evolution of three LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2 discharged composite electrodes of different particle sizes upon cycling (to 3.0 V vs Li/Li^+) (g) 20 cycles, and (h) 100 cycles. The inset shows the magnified semicircle at the high-frequency region in corresponding main figures. After refreshing with a new Li metal anode and electrolyte after 50 cycles, the cell performance and impedance (Supplementary Fig. 17) do not show improvement, confirming the deterioration of the cathode-electrolyte interface being the main reason for the sluggish charge-transfer kinetic properties; meanwhile, a Bode plot of three discharged electrodes after 100 cycles in Supplementary Fig. 18 indicates the interphases on Li anodes contribute to the first high-frequency semicircle.
Passivation of the electrode/electrolyte interface by CEI. We carried out detailed surface chemical and structural characterizations to provide direct evidence of this passivation effect. Compared with the electrode aged for 30 days without any electrical bias applied, the cycled electrode over the same period of time exhibits less amount of CEI species at the surface; in the meantime, high-voltage cycling notably accelerates active mass dissolution (Supplementary Fig. 19). It is expected that the spontaneously formed CEI will partially decompose at the highly oxidizing environment of ~4.5 V. In Fig. 4, we present a quantitative investigation of the surface degradation owing to electrode-electrolyte reactivity during cell operation. Comparison of normalized TOF-SIMS depth profiles of representative CEI signals with ROI-1 (active particles) taken on samples at various cycles (3, 20 and 100) are shown in Fig. 4a and in Supplementary Figs 20–24. Their corresponding calculated CEI formation depth as a function of cycles is illustrated in Fig. 4b. In Fig. 4a,b, we witness a clear correlation between the LiNi0.7Mn0.15Co0.15O2 secondary particle sizes and CEI formation depth (that is, larger particles lead to thicker CEIs). In contrast, such tendencies are reversed for the active mass dissolution products generated per unit area of the active material, which are more severe for the sample with smaller particles (Fig. 4c). Moreover, though collector and separator resistances. The impedances obtained here are mostly indexed to Li-ion migration through surface films formed (spontaneously and electrochemically) on both Li metal anodes and LiNi0.7Co0.15Mn0.15O2 cathodes (that is, the first high-frequency flat semicircle) and charge-transfer across the cathode active-material/surface-film interface (that is, the second semicircle at medium-to-low frequency range). Often, the interphasial species, such as ROCO2Li (refs 5,33) and LiF (ref. 42), are highly resistive and yet enable facile Li diffusion during the intercalation process, while the interfacial charge transfer dominates and becomes greatly hurred by the combined impacts of active mass dissolution and structural reconstruction at the particle surface. Indeed, the first semicircles are almost invisible compared with the second ones in the figure, indicative of negligible adverse kinetic impacts of CEI on Li-ion insertion/extraction. For each cell, the Li-ion transport appears more rapid for the sample of smaller particles, which can be ascribed to less CEI formation on the sample with larger surface area (Fig. 3b); meanwhile, a larger downward trend in the charge-transfer kinetics is observed. This explains the difference in cell performance among three samples in Fig. 3d-f and suggests that the CEI leads to suppression of the electrode/electrolyte interface deterioration during high-voltage battery operation.
damaged initially, the CEI appears somewhat stabilized during repeated charge-discharge cycles, whereas the dissolution products accumulate drastically. X-ray photoelectron spectroscopy (XPS) analysis in Fig. 4d reveals the interphases on cycled LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2 electrodes similar to those reported in the literature on layered transition-metal oxides \cite{9,18,23,30} and further corroborates the differing degree of surface degradation among electrodes of different secondary particle sizes. The Ni 2p, F 1s, O 1s and C 1s regions high-resolution XPS spectra of representative pristine, aged and cycled electrodes, as well as pure NiF_2, are depicted. The O 1s region reveals a native film mostly consisting of Li_2CO_3 on the LiNi_{1-x}Mn_xO_2 pristine particles, and various

Figure 5 | Quantification of surface degradation due to structural reconstruction. (a–h) Images of LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2 particles surface after 100 cycles at room temperature: (a–d) 8–10 μm and (e–h) 18–20 μm. (a,e) High-resolution transmission electron micrographs illustrating the secondary particle morphology. (b,f) Magnified corresponding locations at a primary particle surface marked by a red dot in a,e with insets of fast Fourier transform patterns of regions divided by a dashed line. These patterns show the rock-salt phase, that is, Fm3m [110] zone axis (in blue), and the pristine layered phase, R3m [100] zone axis (in orange), respectively. (c,g) HAADF-STEM images of areas enclosed by a red rectangle in b,f indicating the local atomic arrangement along the interface region. (d,h) Corresponding HAADF signal profiles of the blue and orange dashed lines in c,g providing additional evidence of the different structures neighbouring the interface region. The scale bars in a and e, b and f, c and g are, respectively, 1 μm, 20 nm and 2 nm. Note that the CEI is largely invisible in these images owing to the destructive effect of high-energy electron-beam irradiation during STEM characterization\cite{46}.
Electrolyte degradation products \(^{18,24}\) are generated during aging, such as semicarbonates, LiF, MF\(_x\), Li\(_x\)PO\(_4\)F\(_2\) and RCF\(_x\). In this study, as mentioned above, we focus on certain interphasial species that are mainly produced from spontaneous reactions between carbon black and LiPF\(_6\)/EC-DEC (defined as the CEI here) and active mass dissolution products instead of those from other origins. For cycled electrodes, reduction in the amount of CEI species is noticed compared with the aged one (Fig. 4d). In support of TOF-SIMS results, the degree of dissolution products generation (NiF\(_2\)) at the electrode surface is found larger for the sample with smaller secondary particles (Ni 2p, 8–10 μm); meanwhile, the CEI formation appears more pronounced for the sample with larger particle size (C 1s and O 1s, 18–20 μm). However, such comparison should be treated with caution, since XPS cannot selectively retrieve data from the interphases on the active material.

Another essential aspect of surface deterioration, that is, formation of the surface rock-salt phase (NiO) owing to intrinsic structure reconstruction, was also quantitatively analysed for LiNi\(_{0.7}\)Co\(_{0.15}\)Mn\(_{0.15}\)O\(_2\) electrodes cycled under similar conditions. In Fig. 5, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images are displayed for samples of 8–10 and 18–20 μm in secondary particles size. The two distinct regions of the rock-salt Fm3m and the original layered R3m structures, divided by a dashed line in Fig. 5b,g, are confirmed by corresponding fast Fourier transform patterns (Fig. 5b,g insets) and high-resolution HAADF images/signal-profiles taken at the interface region\(^{19,21,22}\) (Fig. 5c,d,f,h). As seen, the rock-salt phase becomes significantly thick after 100 cycles along lithium slabs (where Li-ion diffusion is more rapid) for both samples, and is featured by a porous structure from a clear difference in contrast between the outer surface and the inner bulk areas. This suggests that the highly localized active mass dissolution products form in corrosion pits, and are largely overlapped with the rock-salt phase regime at the surface. Note that it is generally challenging to spatially resolve these dissolved transition-metal species in high-resolution STEM characterization. HAADF-STEM patterns of pristine samples free of the electrochemically induced rock-salt phase can be found in Supplementary Figs 27–29. As seen, the extent of rock-salt phase formation for the two samples shows a similar tendency to that of dissolution products (Fig. 4c). TOF-SIMS depth profiles of referenced ratios between \(^{58}\)NiO\(^-\) and \(^{56}\)Ni\(^-\) (Supplementary Fig. 30), as well as XRD data for the three cycled electrodes (Supplementary Fig. 15)—both of which can indicate the NiO formation—are in line with the HAADF-STEM results as well.

**Discussion**

On the basis of above results, we conclude that before electrochemical operation, conductive carbon additives (carbon black) readily react with the LiPF\(_6\)/EC-based electrolyte upon contact, giving rise to a CEI that further evolves during cell operation and passivates the LiNi\(_{0.7}\)Co\(_{0.15}\)Mn\(_{0.15}\)O\(_2\) particles. By applying ROI analysis on the TOF-SIMS spectra, we show that this in situ generated CEI originates from the mutual exchange of interphasial species between the active cathode particles and carbon (Fig. 6). Undesired electrode-electrolyte interactions upon battery operation, however, cannot be entirely excluded due to incomplete CEI coverage, which also becomes further compromised in strongly oxidizing conditions up to 4.5 V vs Li/Li\(^+\). Moreover, we provide direct evidence of the overall protective nature of the CEI at cathode particles surface upon cycling, via TOF-SIMS, XPS and HAADF-STEM. By employing samples of different secondary particle sizes, we are able to alter the CEI thickness. For a fixed amount of carbon in the electrodes (10%), a thicker CEI adheres onto the active material with a smaller relative surface area (larger particles) during aging. Meanwhile, an unequivocal correlation between the thickness of CEI and the generation of degradation products is revealed among the three LiNi\(_{0.7}\)Co\(_{0.15}\)Mn\(_{0.15}\)O\(_2\) samples (Figs 3b, 4b,c and 5). The results show the spontaneously deposited CEI somewhat stabilizes during repeated cycling up to 4.5 V and to some extent suppresses the active mass dissolution and structural reconstruction at the particles surface, in good agreement with the impedance data in Fig. 3g.h. The evolution of CEI in thickness is similar to the observation of solid-electrolyte interphase growth on graphite\(^ {33}\).

It is worth noting that the contribution of conductive carbon additives to the surface chemistry is not limited to composite cathode electrodes. Although different (oxidation and reduction) reactions are involved, the puzzling similar interphasial species identified on cathodes and anodes\(^ {4,5,9,14,17,18,24,30,31}\) might be in part explained by the use of conductive carbon on both sides. The consistent open-circuit voltage (around 3 V) empirically observed for a broad spectrum of cathode and anode materials against Li metal before cell operation may also be related to the chemical reactivity of conductive carbon towards LiPF\(_6\)-containing nonaqueous electrolytes, which spontaneously produces similar surface deposits on different electrode materials. In addition, the involvement of conductive carbon in the formation and evolution of cathode interphases is quite complex, and this study simply provides an intriguing glance into this phenomenon. To begin with, carbon generally possesses widely varying surface area and a diversity of surface chemical functional groups depending on the manufacturing processes. This can lead to unexpected interactions with the electrolyte and the CEIs generated may not be the same as that described here for different types of carbon additives in various cell chemistries. Further, the passivation effect of the carbon-driven CEI in simple LiPF\(_6\)/EC-DEC solutions is far from ideal. The anodic instability of conductive
carbon, including PF$_5^-$ intercalation$^{30,44,45}$ and direct oxidation$^{31}$ at voltages approaching 5 V vs Li/Li$^+$, also becomes detrimental to cyclability. Modifications on the electrolyte can produce more robust CEIs$^{4,28,29}$, but the detailed functioning mechanisms of these changes are not well understood. Finally, the current study monitors only the CEI evolution in terms of thickness once the electrochemical reactions initiate, rather than the chemical composition and other important properties that are also relevant to the cell performance. Thus, future studies are needed to comprehensively delineate the role of carbon in affecting the surface chemistry of composite electrodes and electrochemical properties of Li-based batteries, which should assist the development of in situ passivation on high-voltage cathode materials.

In summary, our findings reveal the dynamic changes of interphases involving complex, intertwined ‘communications’ between the active cathode material (LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$) and conductive carbon additives in lithium-ion batteries, and their substantial repercussion on the electrochemical properties. Notably, the majority of studies on cathode interphases thus far underestimate the influences from carbon, thereby introducing ambiguities and inconsistencies. Although some have pointed out the need to study a model electrode material surface without the carbon additives and binder$^{14,17}$, in the practical sense, the interphase behaviour only present when the active material and carbon coexist needs also to be emphasized. For example, the interactions of electrolyte additives with carbon itself and/or carbon-driven interphases generated spontaneously in nonaqueous electrolytes may have a role in their effectiveness. The development of tunable and well-controlled in situ surface passivation on electrodes by carbon might also be an alternative approach to mitigate the surface side reactions of high-voltage, high-energy-density cathode materials in lithium-based chemistries, provided that surface functionalization of conductive carbon materials is low-cost and easy-to-use. Conversely, such efforts should at the very least serve to understand and eliminate existing unwanted molecular interactions between the electrolyte and conductive carbon (for example, graphene). Finally, we underscore the benefits of surface-sensitive techniques (such as TOF-SIMS) that enable the spatially selective observation of composite electrodes in understanding the dynamic nature of electrode interphases formation and evolution before and during electrochemical reactions.

Methods

Preparation of LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$. LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ powder was prepared by a two-step method: the transition-metal co-precipitation route and subsequent annealing-induced lithiation process. In the first step, NiSO$_4$·6H$_2$O, CoSO$_4$·7H$_2$O, and MnSO$_4$·H$_2$O were dissolved in distilled water at a combined concentration of 10 mol% Ni$_{2}$Co$_{1}$Mn$_{1}$O$_{2}$ (molar ratio of Ni:Co:Mn = 70:15:15) of 1.0 mol·l$^{-1}$. Then the mixed metal solution was pumped into a 2.51 continuously stirring tank reactor, along with optimized amounts of saturated Ni(OH)$_2$ and KOH aqueous solutions fed separately into the tank under protective gas. During the reaction, the pH (11–11.5), the stirring rate (800–1,000 r.p.m.), the temperature (50–60 $^\circ$C), and the residence time (4–12 h) were controlled and monitored carefully. After the co-precipitation treatment, the resulting product Ni$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_{2}$ was washed thoroughly before drying at 100 $^\circ$C under vacuum overnight. The LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ powder was then obtained by heating the as-prepared compound mixed with LiOH·H$_2$O at a molar ratio of 1:1:3 at 800 $^\circ$C for 15 h in air. The mixture was preheated at 500 $^\circ$C for 5 h before the final heating step.

Electrode fabrication and electrochemical testing. The electrochemical properties of the LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ materials were studied with CR2032-type coin cells. For regular cell testing, the active material, conductive carbon additive (Super P, type of carbon black), and binder (polyvinylidene fluoride) with the weight ratio of 80:10:10, respectively, were mixed and the resulting slurry was coated onto an aluminum foil with ~4 mg·cm$^{-2}$ active material loading. A weight ratio of 88:1:11 was also used during the aging study to investigate the effect of carbon black. The obtained composite cathodes were assembled into coin cells with Li metal as both the counter and reference electrodes in an electrolyte solution of 1 M LiPF$_6$ in a mixture of EC and ethyl carbonate (1:1, v/v). Galvanostatic discharge–charge experiments were registered on a 96-channel battery cycler (Arbin Instruments) between 3.0 and 4.5 V vs Li/Li$^+$ at room temperature. Impedance spectra were recorded on equilibrated cells stabilized after discharging to 3.0 V with the drift in open-circuit voltage no greater than 1 mV for 3 h, using an impedence spectrometer (Solartron 1260 A). In the impedance measurements, the a.c. frequency varied from 0.10 MHz to 2 MHz with a signal amplitude of 5 mV.

Materials characterization. Powder XRD was carried out on a MiniFlex 600 X-ray diffractometer (Rigaku) with Cu K$_\alpha$ (λ = 1.54184 Å) radiation. Scans were collected at 5–80$^\circ$ at a scan rate of 0.5 $^\circ$·min$^{-1}$. Chemical compositions of the LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ samples were determined by an inductively coupled plasma optical emission spectrometer (Varian 715 ES). A NOVA 2000 surface area analyser (Quantachrome Instruments) was employed to obtain the Brunauer-Emmett-Teller surface area of the as-prepared samples. Images of pristine LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ powder and cycled composite electrodes were taken on a Quanta 650 ESEM field-emission scanning electron microscope (FEI) and a S5500 SEM/STEM scanning transmission electron microscope (Hitachi). An aberration-corrected field-emission JEM-2100F scanning transmission electron microscope (JEM-2100F) was also used to identify the local surface structure of cycled cathode materials. STEM images were taken near nickel, cobalt, manganese, fluorine, oxygen, carbon, and lithium regions (0.1 eV step). XPS data of Ni$_2$F$_2$ (Matrix Scientific 99%) was also collected during the experiment. The pressure of the analysis chamber was maintained at around 2 × 10$^{-9}$ mbar. All detected secondary ions of interest had a mass resolution > 5,000 and possessed negative polarity. A pulsed 30 keV Bi$_3^+$ (20 ns) ion beam set in either the High Current mode or Burst Alignment mode (with seven bursts) was applied for depth profiling or high lateral resolution mapping (<200 nm) analysis, respectively. The typical analyzed area was 100 × 100 μm$^2$. A 500 eV Cs$^+$ ion beam (spattering rate estimated at ~0.03 nm s$^{-1}$, calibrated by a pristine LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ composite electrode) was used for sputtering of the cycled composite electrodes or shallow milling of the cross-sectioned samples with a typical sputtered area of 300 × 300 μm$^2$. The XPS and TOF-SIMS analyses, all samples were rinsed in dimethyl carbonate and dried in an argon-filled glovebox, and then transferred to the instruments with a novel air-free interface (U.S. Patent Application Serial No. 14/445,650 filed 29 July 2014).

Data availability. The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions
W.L. and A.M. conceived the experiments. W.L. carried out the material synthesis and electrochemical work. W.L. and A.D. designed the TOE-SIMS characterization and data analysis. H.C. conducted the XPS measurement. P.O. and J.C. developed and S.P. performed the HAADF-STEM characterization. W.L. and A.M. and D. wrote the paper with input from all authors. A.M. supervised the project.

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