

Unravelling the Mechanism of Pulse Current Charging for Enhancing the Stability of Commercial $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ /Graphite Lithium-Ion Batteries

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The key to advancing lithium-ion battery (LIB) technology, particularly with respect to the optimization of cycling protocols, is to obtain comprehensive and in-depth understanding of the dynamic electrochemical processes during battery operation. This work shows that pulse current (PC) charging substantially enhances the cycle stability of commercial $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532)/graphite LIBs. Electrochemical diagnosis unveils that pulsed current effectively mitigates the rise of battery impedance and minimizes the loss of electrode materials. Operando and ex situ Raman and X-ray absorption spectroscopy reveal the chemical and structural changes of the negative and positive electrode materials during PC and constant current (CC) charging. Specifically, Li-ions are more uniformly intercalated into graphite and the Ni element of NMC532 achieves a higher energy state with less Ni–O bond length variation under PC charging. Besides, PC charging suppresses the electrolyte decomposition and continuous thickening of the solid-electrolyte-interphase (SEI) layer on graphite anode. These findings offer mechanistic insights into Li-ion storage in graphite and NMC532 and, more importantly, the role of PC charging in enhancing the battery cycling stability, which will be beneficial for advancing the cycling protocols for future LIBs and beyond.

1. Introduction

Over the course of 30 years' development of lithium (Li)-ion batteries (LIBs), focus in the field has remained on achieving safe and stable LIBs for electric vehicles, portable electronics, etc.^[1,2] Generally, batteries retaining 80% of their nominal capacity (i.e., 80% state-of-health (SoH)) reach their end-of-life.^[3,4] The nowadays state-of-the-art LIBs are based on $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532)/graphite,^[3] which usually only have a service life of 5 to 8 years.^[3] By optimizing the cycling conditions, LIBs are expected to be in service even for decades,^[5] which will greatly alleviate the pressure on battery manufacturing and recycling, and ultimately enhance the sustainability of our future society.

Advanced charging protocols, e.g., pulse current (PC) charging, hold the potential to prolong the service life of current LIBs.^[6,7] Specifically, PC

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charging with relaxation has been extensively employed in electrochemical testing of NMC/Graphite,^[8–10] LiFePO₄ (LFP)/Carbon-based,^[11,12] LiCoO₂ (LCO)/Graphite,^[13] and LFP/Li^[14] batteries from lab cells to commercial batteries. A typical PC charging protocol consists of a constant current (CC) charging step followed by a relaxation period, and the durations of the charging and following relaxation periods vary depending on the experimental design. These studies have been carried out for batteries with various electrodes (NMC, LFP, and LCO) and battery formats (coin cell, pouch cell, and cylindrical cell) and show promising results, demonstrating the potential of PC charging for improving battery stability by a significant margin, ranging from 0.5% to 34%, as depicted in **Figure 1**. However, mechanistic understanding on how PC charging enhances battery performance remains limited, which hinders the optimization of charging protocols and the advancement of future batteries.

To unravel the performance improvement of LIBs under PC charging, it is of vital importance to understand their aging mechanism during service. The aging mechanisms observed in commercial batteries are primarily attributed to several factors, including polarization resulting from interfacial film thicken, loss of active materials, and loss of Li ions.^[15,16] Our previous work has unveiled the main causes of NMC532/graphite battery degradation, highlighting the crucial role of interfacial film growing and the loss of cathode and anode materials in this process.^[17] A well-known aging mechanism in LIBs is the continuous growth of the solid-electrolyte interface (SEI) on the anode resulting in the depletion of Li supply and capacity decay.^[4,18] Moreover, the presence of SEI hinders the transport of Li-ions, leading to higher interface impedance^[19] and hence larger dis-/charge overpotential during battery operation, ultimately decreasing the achieved capacity.^[20] Furthermore, the NMC532 and graphite electrodes suffer from cracking in structure, along with electrode exfoliation, which also contributes to capacity loss.

In this paper, we show that PC charging can mitigate these issues. While it is difficult to rationalize the approach, a few general arguments can be made. Generally, the diffusion of Li-ions in the electrolyte is much slower than the electron transport in the external circuit and the electrodes. The slower Li-ion diffu-

sion compared to electron transport results in concentration polarization of Li-ions within the battery.^[3] Consequently, this uneven distribution leads to the depletion of Li-ions and accumulation of solvent molecules and anions near the electrode, aggravating the reaction between electrons and solvent/anion to form SEI species.^[6] At the counter electrode (NMC532), the concentration of Li-ions increases. Subsequently, the reduction in solvent concentration becomes a hurdle to amalgamate the extracted Li-ions from the cathode with solvent anions. As a result, this could potentially influence the energy states of transition metals, nickel (Ni) included. In contrast, PC charging allows extra time for ion diffusion to compensate for the imbalance in electron and ion transport. This reduces the polarization and hence the SEI thickening. The reduced polarization may also lower the risk for the graphite electrode to run into Li plating conditions towards the end of the charging process. Besides, the electrode materials undergo structural relaxation between current pulses, which may mitigate the mechanical stress and structural degradation of electrode materials.

To testify the hypothesis, in this work, we study the electrochemical behaviors of 18650-type NMC532/graphite LIBs during aging with different charging protocols: CC or PC. Moreover, through comprehensive electrochemical analysis and a toolkit of post-mortem and *operando* characterization, we comprehend in detail the electrochemical processes of Li-ion storage in NMC532/graphite and SEI formation under CC and PC charging. These results contribute to unraveling the mechanism of enhanced cycling stability under PC charging.

2. Results and Discussion

2.1. Battery Performance and Electrochemical Diagnostics

As shown in **Figure 2a**, the NMC532/graphite battery charged at constant current retained only 37.8% of its initial capacity after 1000 cycles, and stopped service (i.e., 80% SoH) after only 500 cycles. In sharp contrast, the batteries charged with pulsed current exhibit much enhanced cycling performance over cycling. In particular, at a pulsed current with a frequency of 100 Hz (denoted as Pulse-100), the battery's capacity retention rate reaches 66.48% after 1000 cycles with a cycle life of >700 cycles. And, at a 2000 Hz pulsed current (denoted as Pulse-2000), the capacity retention rate of the battery is as high as 81.73% in 1000 cycles, i.e., more than twice the cycle life compared to that at CC charging. Obviously, the PC charging method effectively improves the battery cycling performance. It is worth noting that the battery under CC charging remains relatively stable during the initial 400 cycles but experiences accelerated degradation afterward. This is consistent with the reported aging trajectory of commercial LIBs,^[21] which consistent of three stages along cycling: initial capacity fading related to SEI growth and anode material loss, gradual aging due to the loss of active materials, and accelerated degradation caused by the synergistic effects of the processes. **Figure 2a** shows that PC charging greatly extends the gradual battery degradation (i.e., the second stage) and thus inhibits accelerated battery aging (i.e., the third stage) over long-term cycling. In our previous report,^[17] it has been revealed that the aging mechanisms under CC charging is the increased interfacial impedance and polarization, especially on the graphite anode, and loss of active materials. PC

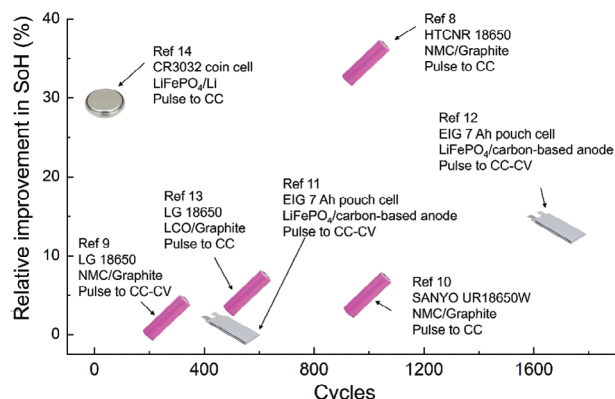


Figure 1. Relative improvement in SoH of Li-based batteries under pulse current charging compared to continuous current charging protocols (CC: constant current; CV: constant voltage).

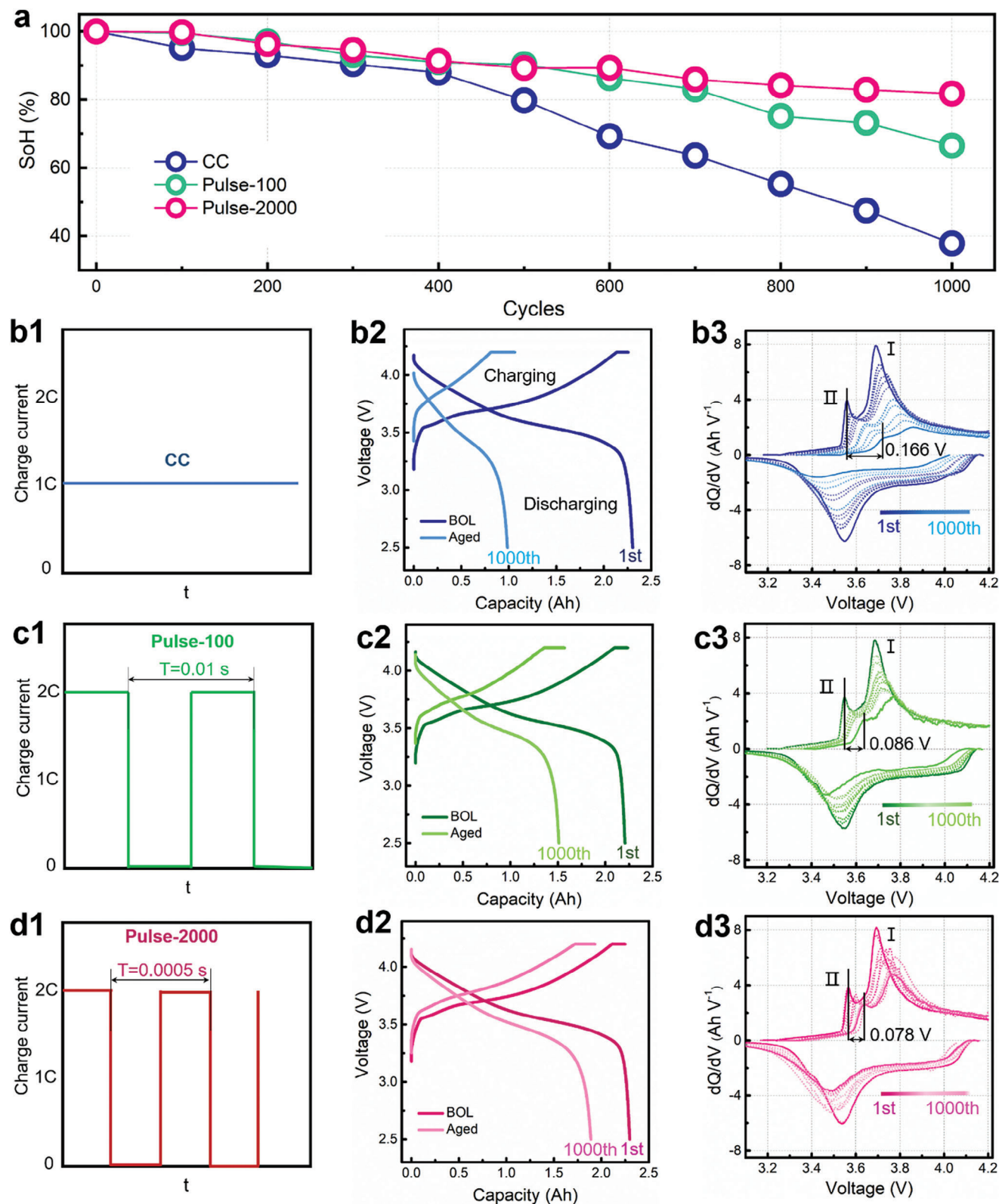


Figure 2. Electrochemical behaviors of the reference performance tests (RPTs) for 18650-type NMC532/graphite LIBs aged with different charging protocols: CC, Pulse-100, and Pulse-2000. The RPT rests were performed after every 100 cycles of battery aging. a) The battery SoHs obtained from the RPTs during aging. The current wave shapes for battery aging, and the dis-/charge voltage profiles and IC curves of the RPTs for batteries aged with b1–b3) CC, c1–c3) Pulse-100, and d1–d3) Pulse-2000 charging protocols. BOL: beginning of life.

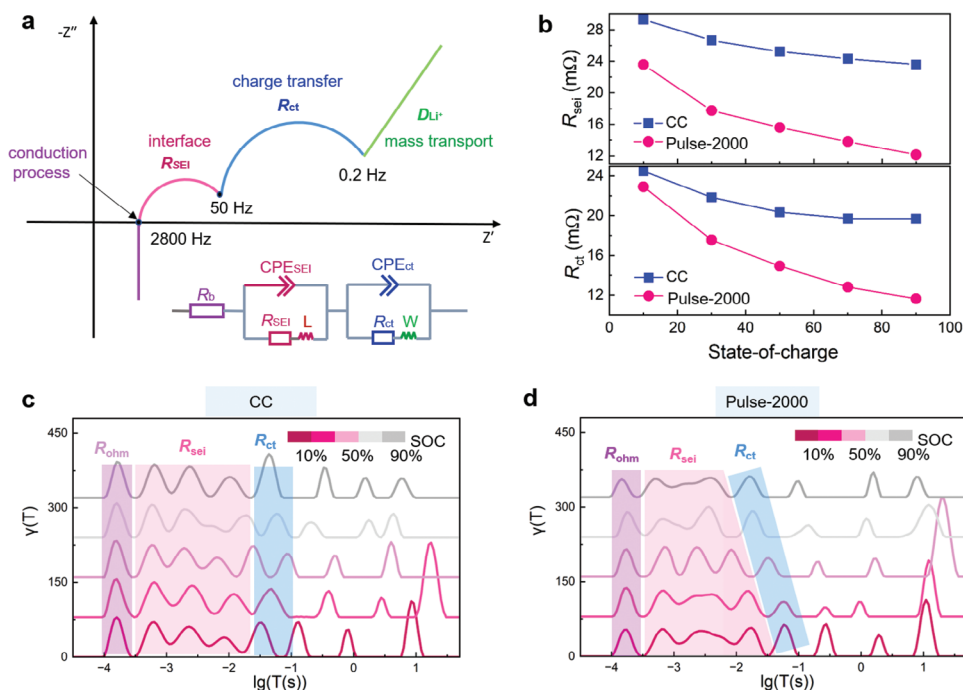


Figure 3. EIS results of the batteries after aging for 1000 cycles under CC and Pulse-2000 charging. a) The characteristic Nyquist plot and equivalent circuit diagram, b) the fitting results of R_{sei} and R_{ct} in relative with the SoC; The distribution of relaxation time (DRT) profiles at 10%, 30%, 50%, 70%, and 90% SoC for the batteries aged under c) CC and d) Pulse-2000 charging. The regions marked with colors are related to the major electrochemical processes in batteries, namely Ohmic resistance (purple) and across the SEI (pink), and charge transfer (blue), respectively.

charging alleviates accelerated battery aging by suppressing the loss of active materials and interface impedance increase. Comparing the charging and discharging curves under these three charging methods (Figure 2b2–d2), it shows a rising tendency of the charge voltage and a dropping trend for the discharge voltage over 1000 cycles. This is most evident for the CC-charged battery and is related to battery polarization.^[17] The battery polarization is reduced when charged with a pulse current, and further decreases as the pulse frequency increases from 100 to 2000 Hz. The shift of the secondary peak (peak II) in the incremental capacity (IC) curve is a useful parameter for quantifying the increase in polarization.^[22] Here, the peak II shifts by 0.166, 0.086, and 0.078 V for the batteries charged under CC, Pulse-100, and Pulse-2000, respectively (Figure 2b3–d3). The main peak (Peak I) serves as an indicator for the loss of active materials in both the cathode and anode.^[23] Under CC charging, the peak I gradually diminishes and can nearly vanish after ≈ 1000 cycles, reflecting the substantial loss of active materials from the electrodes. In contrast, when using Pulse-2000 charging, peak I remains prominent even after 1000 cycles. This observation suggests that compared to CC charging, the loss of active material is significantly reduced with PC charging. In short, electrochemical diagnosis reveals that the application of PC charging significantly alleviates active material loss and reduces polarization of the battery and a higher pulse frequency results in less battery degradation.

Electrochemical Impedance Spectroscopy (EIS) is an effective method for the identification and analysis of the polarization that takes place within the battery.^[24] A typical Nyquist plot of the EIS data of a battery and the related processes are shown in (Figure 3a).^[25,26] After aging for 1000 cycles, the R_{sei} and R_{ct} val-

ues of the batteries aged at constant current, and Pulse-2000 were measured and shown in Figure 3b (see Figure S1, Supporting Information, for the Nyquist plots). In general, the R_{sei} and R_{ct} decrease as the state-of-charge (SoC) increases, and the resistances of the CC-aged battery are higher than that under PC aging. This is consistent with the much more significant decline of battery capacity during CC aging.

Distribution of relaxation times (DRT) is used to deconvolute electrochemical processes on various time scales from the EIS data at different SoCs. In the interpretation of DRT calculations, specific electrochemical processes (*incl.* charge transfer, interfaces, ion diffusion, etc.) can be distinguished and identified by the time constant (τ) of the corresponding Randles circuit (*i.e.*, RC paralleled circuit—a typical circuit for simulating the interfacial process that consists of an ionic double layer and transport resistances).^[27] The timescale analysis reveals specific kinetic characteristics of the electrochemical processes. In general, charge transfer typically takes place with a time constant between 10^{-2} and 10^{-1} s and Li-ion transport across interfacial films (*i.e.*, SEI and cathode-electrolyte interface (CEI)) occurs between $10^{-3.5}$ and 10^{-2} s.^[28,29] The DRT results (Figure 3c,d) show that the battery aged with CC charging exhibits a longer time constant and hence a higher impedance for interface and charge transfer resistance, compared to that at Pulse-2000. Particularly at a higher State of Charge (SoC), this distinction becomes more pronounced. This phenomenon is attributed to the low porosity of the graphite electrode and the reduced volume fraction of the electrolyte, a consequence of the densely packed graphite particle contacts in high SoC conditions.^[30] As a result, this configuration leads to lower resistance. Besides, the interface resistance, which

is the major kinetic limiting factor for CC sample as proved in our previous work,^[17] is significantly reduced for Pulse-2000. During the charging of NMC532/graphite battery, Li ions are extracted from the NMC532 cathode and intercalated into the graphite anode, which is susceptible to SEI growing on the graphite anode. Besides, the volume of graphite expands during Li-ion intercalation and shrinks during de-intercalation, destabilizing the SEI film and leading to the rupture and continuous growth of SEI. Therefore, the discrepancies of interface resistance under CC and Pulse-2000 charging are mostly associated with the SEI (and not CEI), and the growing SEI film growing under Pulse-2000 charging has a lower impedance. Furthermore, the charge transfer is accelerated in battery aged under Pulse-2000. The time constant of charge transfer under Pulse-2000 charging decreases from 10^{-1} s to 10^{-2} s with increasing SoC from 10% to 90%, while the charge transfer time constant under constant current charging is less influenced by SoC. This observation is possibly related to the porosity formed as a result of the cracking of graphite particles during CC aging.^[30]

Overall, electrochemical measurements (i.e., IC, EIS, and DRT) unveil that PC charging effectively mitigates the increase in SEI and charge transfer resistances, and also alleviates the loss of electrode materials, ultimately leading to an extended battery lifespan. Post-mortem analyses (e.g., XRD, XAS, and SEM) of the aged electrodes allow for direct observation of the loss of active electrode materials related to crystal structure changes and particle cracking, which will be discussed in detail in the following part of this article.

2.2. Mechanism of Electrode Degradation

2.2.1. Degradation Mechanism of Graphite Anode

To elucidate the structural changes in graphite anode under different lithiation protocols, we performed post-mortem analysis and employed ex situ synchrotron X-ray diffraction (XRD) to reveal the crystal structures of graphite electrodes after aging for 1000 cycles under CC and PC charging protocols. The XRD patterns of fresh and aged graphite electrodes in Figure 4a show similar positions for all crystalline peaks of graphite, including the major diffraction peak from the (002) lattice plane, indicating that the layer spacing of graphite remains unchanged after battery aging.^[31] Besides, as the battery ages, the (002) peak broadens significantly, with notable increase of the full width at half maximum (FWHM) for all the aged graphite electrodes, as shown in insert picture of Figure 4a, indicating cracking or even pulverization of graphite particles.^[32] In particular, the increase of the FWHM for graphite electrodes aged under pulsed current (4.12×10^{-3} Å for Pulse-100 and 4.01×10^{-3} Å for Pulse-2000) is less significant than the CC-aged electrode (4.38×10^{-3} Å), and as the frequency of the current pulse increases the FWHM decreases, which suggests that charging with the pulsed current mitigates structure degradation. Particle cracking causes an increase in the internal porosity of the electrode, consequently leading to an increase in the electrode thickness. As a result, the thickness of graphite electrode increases by $\approx 15\%$ (115 μm vs 100 μm for pristine electrode) after aging under 2000 Hz PC charging, which is significantly less than that under CC charging (35%, 135 μm

vs 100 μm) (Figure 4b). The cross-section FE-SEM images are shown in Figure S2 (Supporting Information).

To further unravel the structural evolution of the graphite anode in LIBs during cycling and the influence of the charging protocol, *operando* Raman spectroscopy was utilized to monitor the real-time evolution of the graphite structure during lithiation under constant and pulsed current, respectively. Usually, graphite undergoes complex phase transition during Li-ion intercalation, resulting in various intermediate states, such as LiC_{48} , LiC_{24} , LiC_{18} , LiC_{12} , LiC_6 .^[33] The arrangement of Li ions in graphite inherently strives to achieve a state of lower energy due to the maximized interaction between the embedded Li ions and the graphite host.^[33] *Operando* Raman spectroscopy can capture the subtle changes in structure during lithiation which occurs from 1.0 to 0.003 V versus Li^+/Li . As shown in Figure 4c, during CC lithiation, the voltage profile displays four distinct stages. At stage I, graphite is lithiated to LiC_{48} demonstrating a single G band with a high intensity in the Raman spectrum.^[34] In the following stage (II) where LiC_{48} transits to LiC_{24} then to LiC_{18} , the intensity of the single G band peak decreases and the peak gradually transforms into a doublet band. At stage III (i.e., LiC_{18} to LiC_{12} transition), the doublet peaks decrease in intensity, with the left peak of the doublet becoming significantly weaker. Finally, at stage IV (i.e., transition from LiC_{12} to LiC_6), the doublet band intensity increases. As reported, the doublet G band observed in the Raman spectrum of graphite is related to the unevenly distribution of Li-ions in graphite during intercalation,^[34] which can be mitigated by pulsed current. The *operando* Raman spectra of graphite during PC lithiation are shown in Figure 4d. At stage I and II, the Raman spectra are similar between CC and PC lithiation. During stage III, the doublet peaks undergo a steady decrease in intensity and merge gradually. By stage IV, only low-intensity single peaks remain. The 2 D Raman spectrum of G peak evolution also can be seen in Figure S3 (Supporting Information). The observations imply that Li-ion distribution in graphite during lithiation is more even under pulsed current, as depicted in Figure 4e,f. The thickness of the negative electrode during the lithiation and delithiation processes were measured by an *operando* electrochemical dilatometry. As shown in Figure S4 (Supporting Information), the thickness of the negative electrode experiences significant fluctuations throughout the CC cycling, indicating it is unstable. However, when it comes to PC charging, the thickness variation is notably reduced. This highlights the divergence in the lithium insertion behavior of graphite in these two scenarios. Under PC charging, lithium integration within the graphite becomes more uniform, resulting in reduced volume fluctuations and mitigated mechanical stress that might otherwise lead to graphite fracture.

In short, PC charging facilitates more homogeneous Li-ion distribution in graphite during lithiation and mitigates the cracking and pulverization of graphite particles, effectively suppressing the structural and thickness changes of graphite electrodes in LIBs. Hence, PC charging inhibits the loss of the graphite anode.

2.2.2. Degradation Mechanism of NMC532 Cathode

Post-mortem SEM was performed to study the degradation of the NMC cathodes. As shown in Figure S5a,b (Supporting

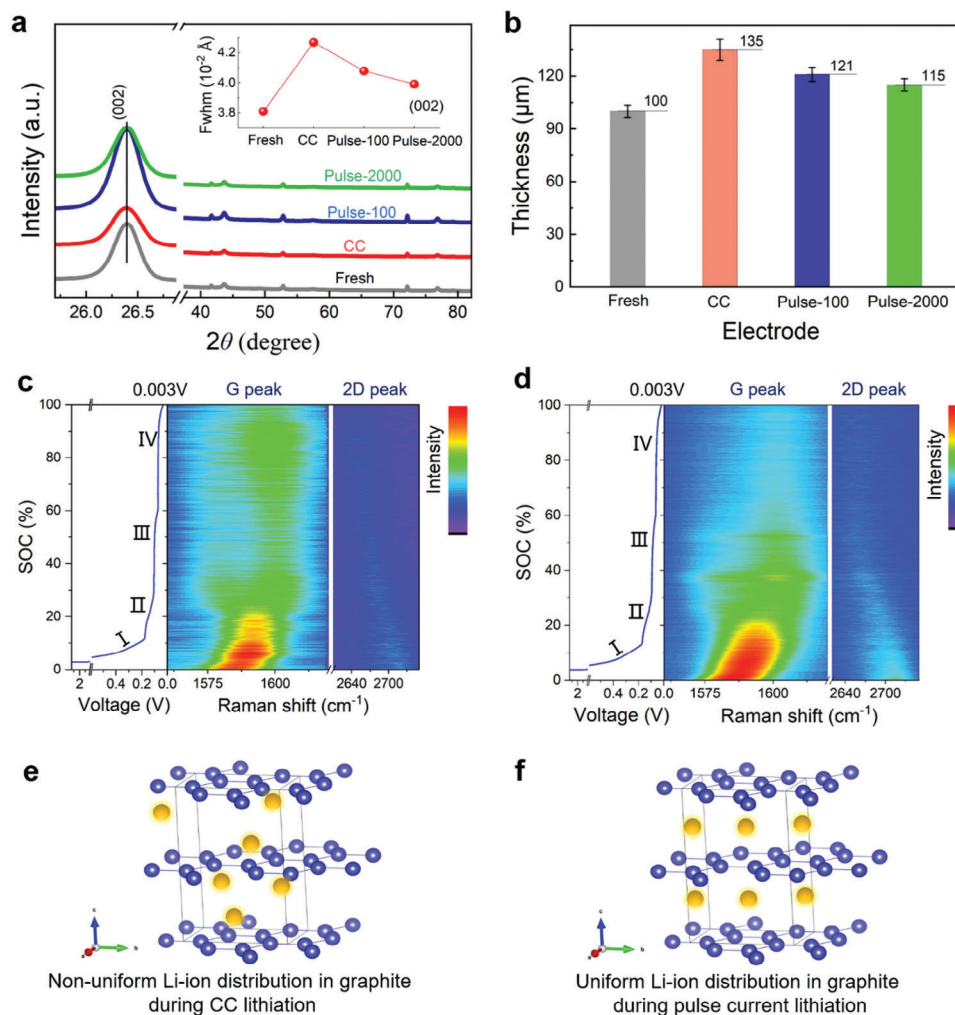


Figure 4. a) Ex situ synchrotron XRD patterns of fresh and aged graphite anode, and the FWHM of the (002) peak of fresh and aged graphite electrodes as inserted picture; b) thickness of fresh and aged negative electrodes based on SEM results; *operando* Raman spectra of the graphite during c) CC and d) pulse current lithiation processes; the state of graphite with Li-ions e) unevenly distribution during CC lithiation, and f) evenly distribution during pulse current lithiation.

Information), there is no significant difference in thickness between the CC and Pulse-2000 aged NMC electrodes. Nevertheless, after CC aging, part of the NMC particles lost contact with and fell off from the current collector, and particle cracking and pulverization was also evident (Figure S5c, Supporting Information), which is caused by the mechanical stress during repetitive Li-ion insertion and extraction processes.^[35] In contrast, the structure and morphology of the Pulse-2000 aged NMC electrode remained largely intact (Figure S5d, Supporting Information).

To further study the degradation of NMC cathode, ex situ synchrotron XRD and ex situ X-ray absorption near-edge structure (XANES) were employed for detailed crystallographic analysis of fresh and aged NMC532 cathodes. Ex situ synchrotron XRD reveals in detail these structural deteriorations. As shown in Figure 5a, the leftward shift of the (003) peak in the CC aged electrode indicates an expansion of the crystal volume or layer spacing in NMC532 materials.^[36] Moreover, the lower intensity of the (018)/(110) double split peak under CC charging than that under PC charging suggests a reduction in crystallinity.^[37] The

Ni–O bond length (Radial-distance) in the aged positive electrode is significantly shortened (Figure 5b). This can be attributed to stronger interaction between O and Ni in higher oxidation states (Ni^{3+} and Ni^{4+}).^[38] Furthermore, the peak intensity of the EXAFS is positively correlated with the coordination number.^[39,40] After aging, Ni exhibits a higher coordination number with oxygen atoms, particularly for the electrodes aged under CC charging, which shows a higher coordination number than that under PC charging. Therefore, PC charging aging results in less high-valent nickel oxides compared to CC charging.^[41] These observations indicate that PC charging is beneficial for preserving the crystallinity and layered structure of NMC532 cathode materials.

To comprehend the aging mechanism of NMC532 cathodes in LIBs, we utilized operando Ni k-edge X-ray absorption spectroscopy (XAS) to investigate the local chemical environment of Ni atoms under CC and 250 Hz PC charging (Figure S6, Supporting Information). In Figure 5c, the Ni K-edge XANES exhibits a rightward shift during the initial charging of the battery, followed by a leftward shift to a lower energy position during discharge.

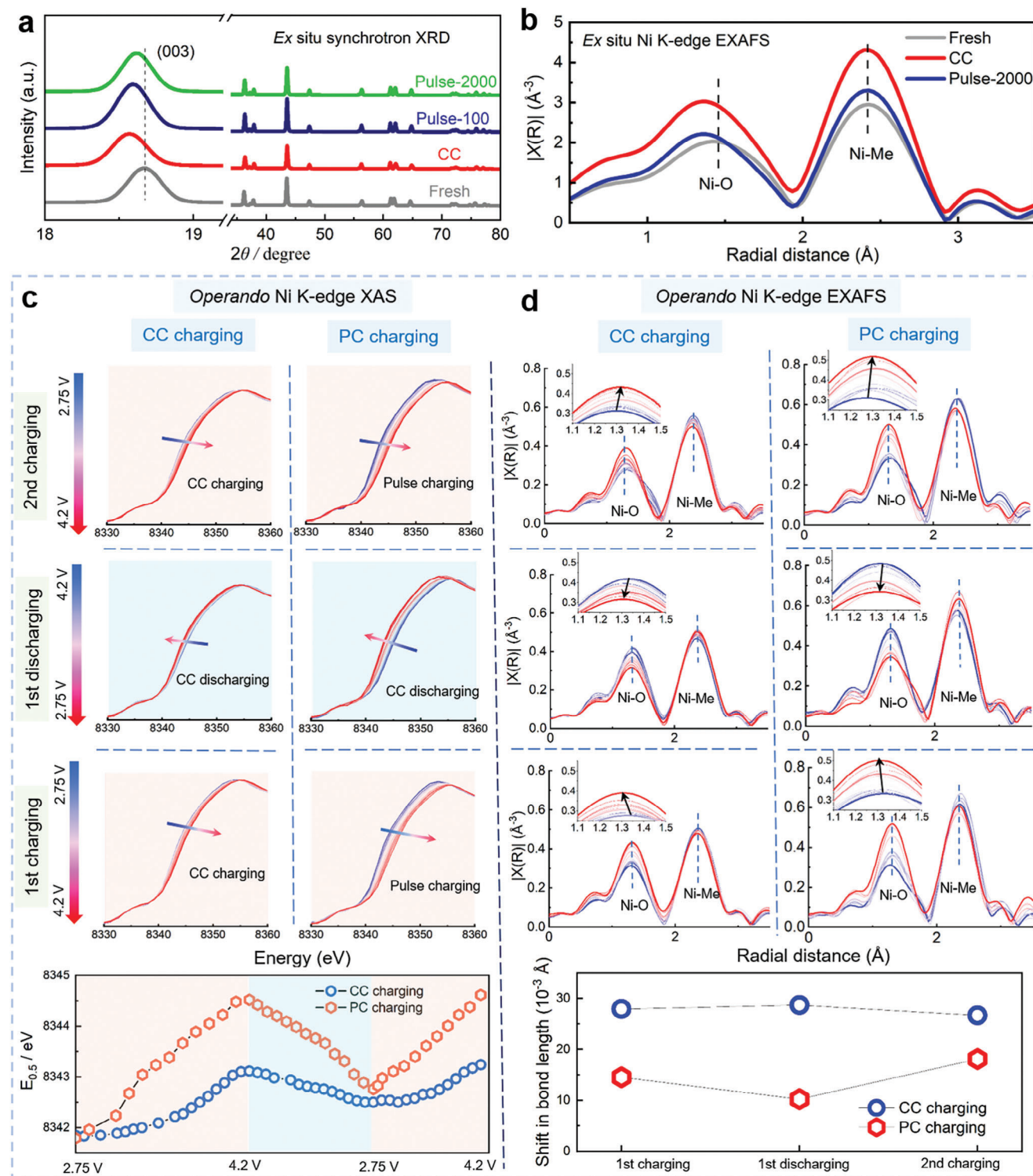


Figure 5. Ex situ synchrotron XRD results for fresh and aged NMC cathodes (a), and Ni K-edge ex situ EXAFS (b); operando XAS for fresh positive electrode under CC and pulse current charging protocols; c) the Ni K-edge XANES evolution of NMC532 during battery charging and discharging with CC and pulsed current; d) the operando Ni K-edge EXAFS and Ni–O radial distance under CC and pulse current charging.

This shift is attributed to charge compensation achieved through the redox process between Ni^{2+} and Ni^{4+} ions.^[42] Compared with that under CC charging, the shift of Ni edge under PC charging is more obvious, indicating the energy and valence states of Ni element change more significantly. The quantified results are shown in the bottom of the Figure 5c. Under PC charging, the Ni element trends to attain a higher energy and valence compared to that under CC charging.

Furthermore, operando Ni k-edge EXAFS was employed to correlate the charge state with the changes in the intensity of Ni–O and Ni-transition metal (Ni-TM) bonds, as shown in Figure 5d. During the 1st charging process, the intensity of the Ni–O peak continuously increases, while the Ni-TM peak displayed an opposite trend, since the Ni valence increase during the delithiation of NMC532 results in more oxygen coordination. Similarly, in the followed 1st discharging and 2nd charging process, the peak intensity of Ni–O and Ni-TM changes more significantly under PC charging than that under CC charging. Particularly, the bond numbers between Ni and transition metals exhibited minimal changes after the initial charge. This is consistent with the energy change of the Ni edge, and the NMC material shows a greater degree of coordination number change under PC charging, which means that the Ni valence will achieve a higher valence state in PC charging. Additionally, the Radial-distance shifts of the Ni–O bond under CC and PC charging are depicted in the inserted pictures. The length of the Ni–O bond undergoes fluctuations with changes in the Ni valence state during charge and discharge. When comparing PC charging to CC charging, the shrinking of the Ni–O bond length is less pronounced in the former, indicating a more stable structure during redox reaction process. This result provides a deeper understanding of the reduced structural deterioration observed in the PC aging case.

In short, the ex situ XRD results unveil that the degradation of cathode materials primarily manifests as an increase in cathode crystal volume and a decrease in the crystallinity of NMC532 cathode materials. Additionally, ex situ Ni K-edge EXAFS further discloses that these deteriorations are closely linked to the formation of Li vacancy phase featuring high valence Ni–O bonding. As summarized in Figure S7 (Supporting Information), PC charging mitigates this process. Additionally, operando XAS highlights the similarities and differences in the valence state, energy, and coordination of Ni atoms in NMC532 under CC and PC charging. PC charging enhances the growth of the valence state of the Ni element, while the fluctuation of the bond length between Ni and O diminishes during battery charging. The moderate changes in structure and Ni–O bond length induced by PC charging could be explained for the overall deterioration of the electrode structure.

2.3. Degradation in Graphite-Electrolyte Interface

PC charging has been demonstrated based on the electrochemical analysis to reduce the growth of interfacial resistance, particularly related to the SEI on the graphite electrode. As shown in Figure 6a, the Raman spectra of graphite anodes show insignificant graphite D, G, D' and G' peaks, due to the surface coverage of the SEI layer on graphite. In addition, other hetero-

geneous peaks appear in the region between 1800–2500 cm^{-1} , which are from the $\text{Li}_x\text{P}_y\text{F}_z$ compounds.^[43] In comparison to the CC-aged sample, the Pulse-2000-aged one exhibits sharper graphite peaks, indicating better crystallinity of the graphite, and, on the other hand, a thinner surface film (SEI) as the latter would allow more light to pass. Indication for the latter process was obtained by scraping-off the graphite particles from the electrode and re-measuring them with Raman spectroscopy. Distinct graphite peaks were observed in the Raman spectra for both the surface-removed CC and Pulse-2000 samples, as shown in Figure 6b. It is noticeable that the $\text{Li}_x\text{P}_y\text{F}_z$ peaks representing the SEI film disappear, proving the presence of a surface film that covered the original graphite electrodes that affects the reflection of 532 nm laser.

Cross section SEM images of the electrodes were recorded to study the surface film. As shown in Figure 6c, the CC sample has ruptured interfacial films on and between the graphite particles. The rupture of these films is likely related to the mechanical stresses occurring during charging/discharging of the cell. Figure 6d shows a distinct passivation film that appeared on the graphite particles surface in the CC sample. In contrast, the Pulse-2000 sample has no obvious passivation film on and between graphite particles, as shown in Figure 6e. This is consistent with the finding from the electrochemical analysis that the SEI growing under CC charging is less stable compared to that under PC charging. Figure 6f shows a thin and undefined film (i.e., SEI) adhering to a graphite particle. This supports the assumption that the PC charging mitigates thickening of the SEI film. The SEI film in Figure 6d was further imaged at a higher magnification and analyzed with EDS mapping of O and C elements, as shown in Figure 6g. The SEI film with uneven thickness is distributed around the edges of the graphite. The SEI film region is consistent with the O element distribution region.

Transmission Electron Microscopy (TEM) was used to investigate the thickness of SEI film. As shown in Figure 6h, no clear surface film is observed for the graphite anode from fresh battery. An SEI film of ≈ 110 nm and < 50 nm is present on the CC- and PC-aged graphite anode, respectively (Figure 6i,j), indicating that PC charging suppresses the growth of the SEI film. In comparison, no obvious CEI film is observed on the NMC cathode under both CC and PC charging (Figure S8, Supporting Information), which may be due to the dissolution and migration of CEI films.^[44]

To further investigate the growth of the SEI, XPS with depth profiling was used, applying etching times of 0, 50, and 100 min for the pristine, CC-aged, and Pulse-2000-aged graphite electrodes. Quantitative results of the chemical composition of SEI based on Li_2CO_3 , C=O (e.g., $\text{R-CH}_2\text{OCO}_2\text{Li}$ and $-(\text{CH}_2\text{CH}(\text{OC}(\text{O})\text{CF}_3))_n-$), C–O (e.g., $\text{R-CH}_2\text{OLi}$ and $-(\text{CH}_2\text{CH}_2\text{O})_n-$), LiF, and $\text{Li}_x\text{PO}_y\text{F}_z$ ^[17,45] are shown in Figure 7a and the depth-dependent XPS for O 1s and Li 1s are shown in Figure S9 (Supporting Information). In consecutive XPS etching from 0 to 100 min, the fresh electrode exhibited a highly similar chemical composition. This could be due to the relatively thin SEI of the fresh electrode, where the first etching has penetrated the SEI film. Under CC aging conditions, the LiF content increases significantly with the growing etching depth, indicating a thick SEI film. The second etching result of the PC-aged graphite electrode closely resembled the third etching result, suggesting it is

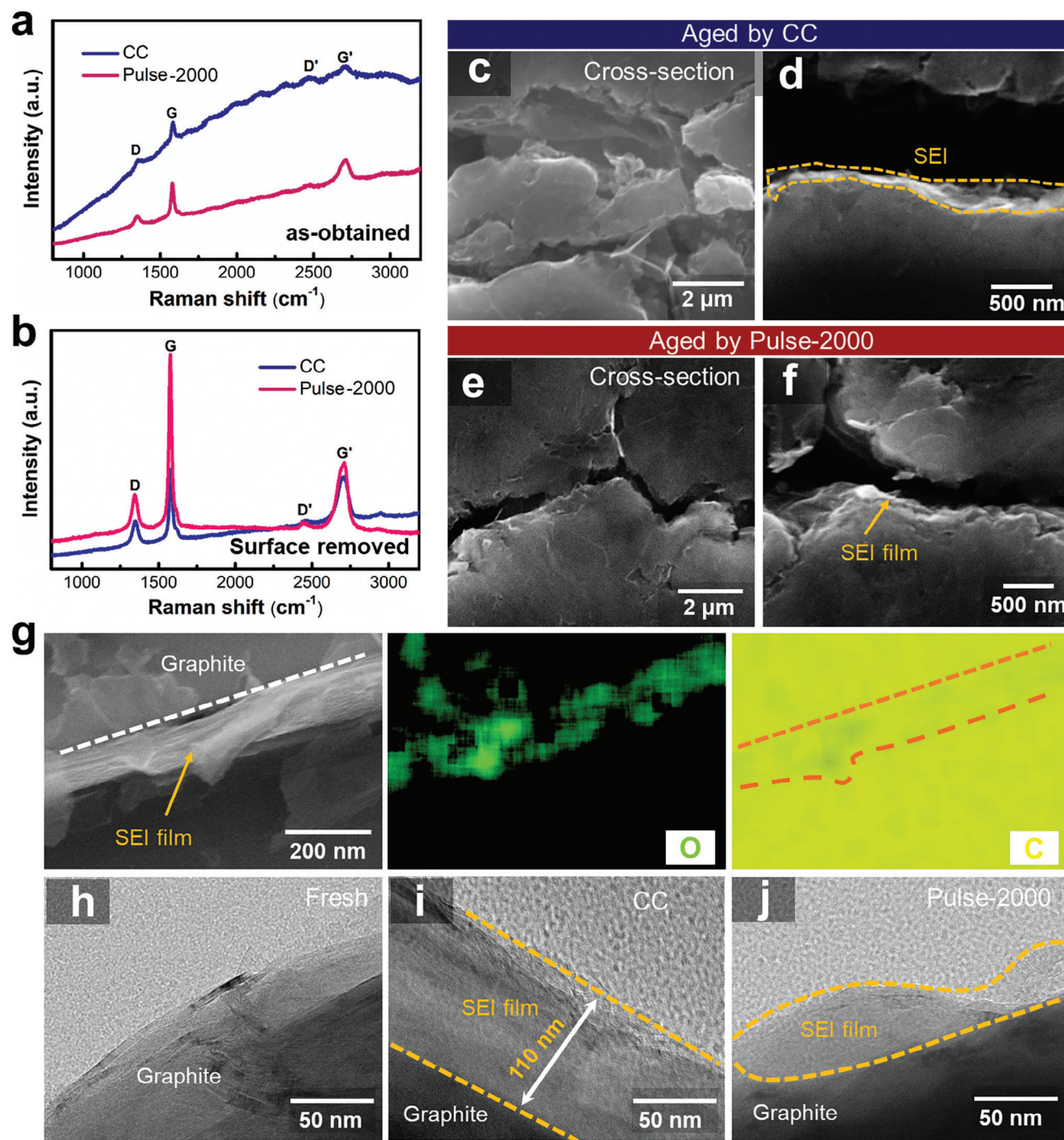


Figure 6. Raman spectra of a) as-cycled and b) surface-removed graphite anodes aged under CC and Pulse-2000 charging. FE-SEM images of the cross-sections of graphite electrodes aged with CC (c,d) and Pulse-2000 (e,f) charging. d,f) are edge-magnified images of (c,e). g) shows the micrograph and O and C element mapping of the surface of CC-aged graphite electrode. TEM images of h) fresh, i) CC, and j) Pulse-2000 aged graphite anodes.

thinner than the SEI in the CC case. This is consistent with the results observed through SEM.

Additionally, compared with the SEI film on fresh and Pulse-2000 graphite electrode surface, the CC-aged electrode has SEI with a higher percentage of Li₂CO₃ at each etched depth. Li₂CO₃ is produced as a reaction product of semi-carbonates decompo-

sition (e.g., lithium ethylene dicarbonate (LEDC)).^[46] After aging of the batteries, inorganic components such as Li₂CO₃ and LiF accumulate on the graphite surface. These compounds are generally brittle,^[47,48] and will cause the SEI film to continually rupture and reform during cycling. The SEI debris accumulates on the graphite surface, resulting in a porous and thickened SEI film.

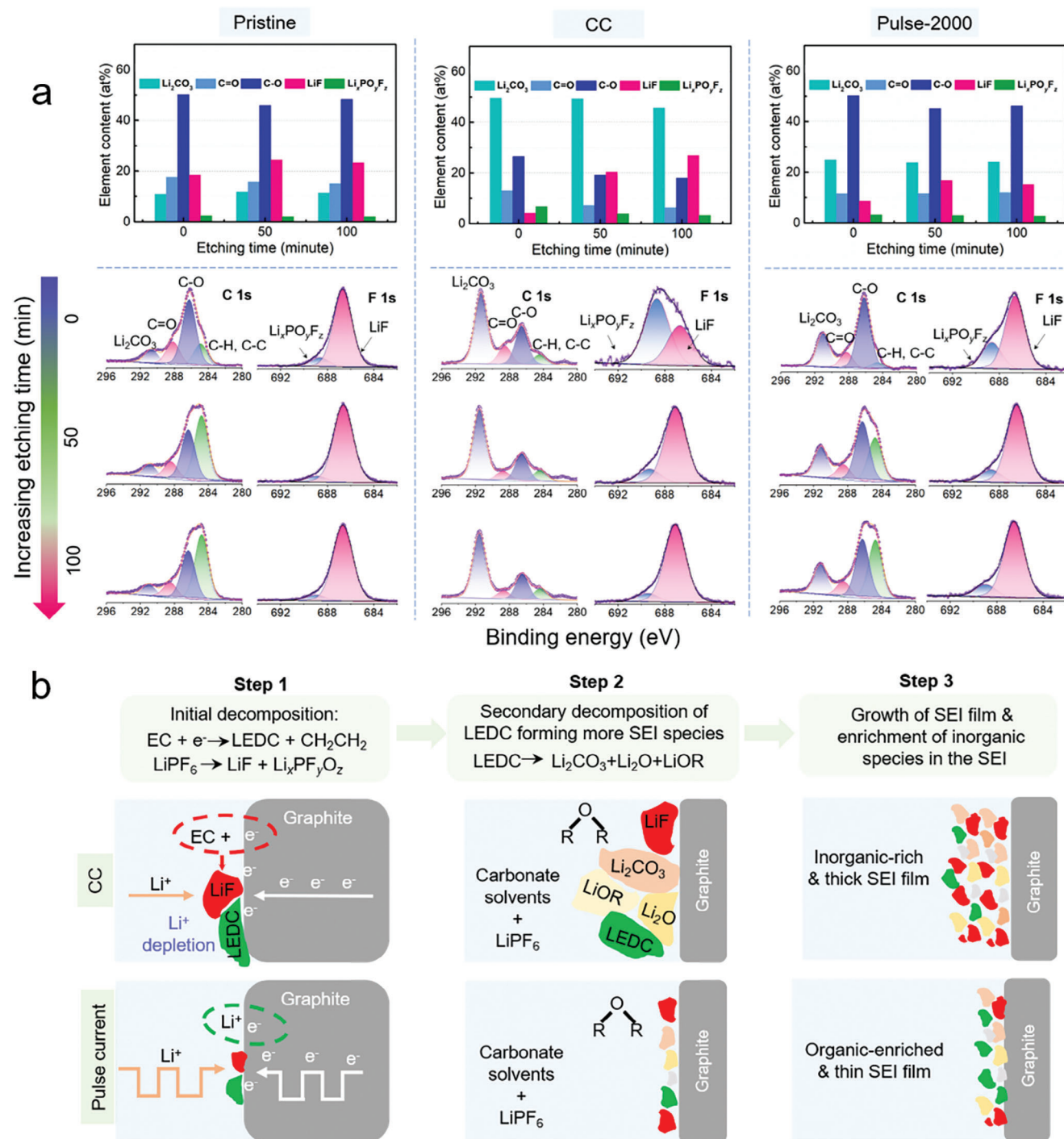


Figure 7. XPS results of the interfaces of graphite electrodes. Chemical compositions of SEI obtained by quantitative XPS characterization of fresh, CC-aged, and Pulse-2000-aged graphite electrodes, and the detailed C 1s, F 1s, O 1s, and Li 1s XPS spectra of graphite electrodes with different etch durations (a). The mechanism of SEI film growing at the graphite interface under constant current charging and pulse current charging based on the demonstration of the above SEM, EDX, and XPS results (b).

Inorganic compounds are less abundant on the surface of the Pulse-2000-aged graphite anode than on the surface of CC-aged graphite indicating again a much slower SEI growth.

Correspondingly, a low inorganic salt content in the SEI implies a relatively high organic content. The content of C–O com-

pounds is much higher on the Pulse-2000-aged graphite surface than that on the CC-aged anode surfaces, which will increase the flexibility of the SEI film to suppress its fracture upon the volume expansion of graphite. As a result, the anode aged under Pulse-2000 charging exhibits a more favorable SEI film.

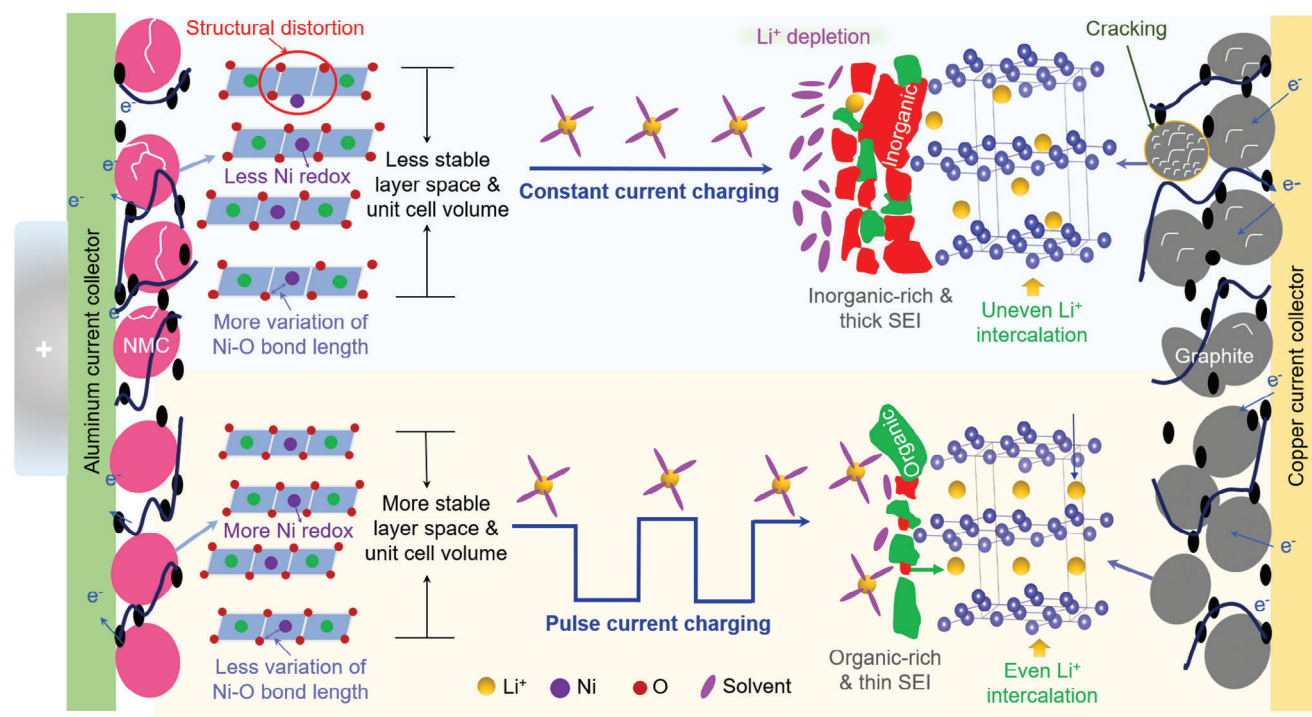


Figure 8. Mechanisms of pulse current charging for stabilizing the cycling performance of commercial NMC/graphite LIBs.

Based on the results of SEM, EDX and XPS analysis, the electrode interface aging modes under PC and CC charging are summarized in Figure 7b. PC charging inhibits the reduction reaction between solvent and interface electrons by balancing the uneven concentration distribution of Li-ions in the electrolyte and reducing lithium depletion at the interface. The SEI formation and growth involves complex chemical reactions, including the decomposition of electrolyte solvent and Li salt and following reactions as below.^[49] During PC charging, both the initial reactions (Equations (1) and (2)) and secondary decomposition (Equation (3)) are inhibited. This slows down the reformation, rupture, and accumulation of inorganic substances (e.g., Li_2CO_3 , LiF, and Li_2O) of SEI, resulting in a thinner SEI film. Overall, the results provide a rational explanation for the reduced increase in interfacial impedance when charging in PC mode.



2.4. Discussion on the Battery Aging Mechanisms and the Influence of Charging Protocols

Based on the above results, we can conclude that there are important differences in the impact of PC and CC charging impacts the properties of NMC532/graphite batteries on various levels.

1) On the cell level, PC charging substantially prolongs the lifespan (cycle life) of batteries. Moreover, the impact of PC charging is influenced by the current pulse frequency. As the cur-

rent pulse frequency increases, e.g., from 100 to 2000 Hz, the battery's cycling stability is notably enhanced.

- 2) On the electrode level, PC charging is effective in reducing the structural changes of graphite and NMC532 electrodes and the impedance of electrode-electrolyte interfaces, especially the SEI film on the graphite anode.
- 3) On the material level, effects of PC charging on NMC532/graphite electrode materials and the electrolyte are demonstrated in Figure 8. a) During Li-ion intercalation with a pulsed current that allows for structural relaxation, the distribution of the intercalated Li-ions in graphite appears more uniform, alleviating the mechanical strain and therefore suppressing the cracking/pulverization and volume expansion of graphite particles. b) PC charging suppresses the formation of structural distortion and amorphization of NMC532, maintaining its crystal structure over cycling. c) PC charging mitigates Li-ion depletion at the electrode-electrolyte interface, thereby altering the electrolyte decomposition and SEI reformation pathway and suppressing second-order reduction of the carbonate-based electrolyte that leads to the formation of inorganic Li salts (e.g., Li_2CO_3). As a result, the SEI layer on the graphite anode appears to be thinner and with a relatively higher ratio of organic compounds resulting from the first-order reduction of carbonate-based electrolyte.

Based on the findings of this study, the high-frequency square-wave current PC charging protocols can be employed to prolong the lifetime of commercial LIBs. To further optimize the charging protocol for battery performance improvement, this effect should be investigated with more influence

factors. This investigation has shown that a rather high frequency of 2000 Hz is beneficial, so testing even higher frequencies could be interesting. However, the pulse frequency should not be higher than the frequency where the impedance becomes inductive, as charging would not take place at such high frequencies. Most probably, the optimal frequency is in the frequency range of the first semicircle. Understanding in detail the relationship between current pulse frequency and electrochemical processes in batteries such as Li-ion movement or SEI growth is crucial to determining the optimal current pulse frequency for stabilizing the battery performance. Also, it is important to address the impact of duty cycle on battery materials, such as Li-ion concentration gradient at interfaces and structural stability of electrode materials, which however requires further detailed studies or simulations. Furthermore, gaining a comprehensive understanding of the structural changes and electrochemical reactions of electrode materials and electrolytes under different charging protocols (e.g., various waveform PC charging^[50,51] and multi-step CC charging^[52]) will facilitate the development of more effective charging protocols.

It is also worth noting that there was no indication for significant lithium plating, which is likely because the experiments were conducted at elevated temperature (35 °C) and at standard currents. At lower temperatures or at higher currents, lithium plating often occurs because the electrode potential can drop below 0 V. However, if charging is done with a high-frequency current, the electrode polarization is lowered which may keep the electrode potential in a safe region.^[53–55] Whether PC charging with relaxation time and multi-step CC fast charging^[52,56] can also inhibit dendrite growth in commercial Li-ion batteries will also be worth to be explored further. Besides, higher currents often accelerate the aging of electrode materials and batteries.^[57] Here, although the peak current under PC charging is twice that of the CC charging, alleviated battery aging is evident, further demonstrating that PC charging can extend battery lifetime.

Furthermore, the mechanism of PC charging for enhancing the cycling stability and cycle life can also be applicable to other types of LIBs, particularly those using transition metal oxide cathode (e.g., LiFePO₄, LiCoO₂, LiMn₂O₄, and other types of NMC) and graphite anode, which undergo similar electrochemical processes during operation.

3. Conclusion

In this study, we show that pulse current charging can significantly enhance the cycling stability of commercial NMC532/graphite batteries and prolong their cycle life (from 500 cycles to >1000 cycles). While the underlying reasons are complex, we shed light on possible mechanisms by using a variety of electrochemical analysis, *operando* and *ex situ* characterization methods at full cell, electrodes, and materials level. The use of PC charging is advantageous in maintaining the stability of electrode materials and interphase and thereby enhancing the battery cycling performance. These findings offer insights for optimizing the charging protocols of nowadays LIBs and beyond during service life and more broadly for the advancement of future battery technology.

4. Experimental Section

Full Cell Test: Commercial 18650-type LIBs (HTCNR18650, nominal capacity: 2200 mAh and voltage: 3.6 V), consisting of Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O₂ (NMC532) cathode and graphite anode, were used for battery aging tests under different charging protocols.

Test platform for battery aging: The batteries were placed and tested in a VT 4002EMC climate chamber with a temperature of 35 °C. The current modes were generated by an analogy output module (type: National Instruments (NI) 9263) controlled by LabVIEW in host computer, then transferred to a KEPCO BOP 100–10 MG bidirectional program for battery power supply. At the same time, an analogy input module NI 9215 was used to measure the voltage and current of the battery, which was connected to a NIcDAQ-9172 Data Acquisition (DAQ) module for data collection. The details can be found in the previous report.^[58]

Aging test procedures: As summarized in Table 1, batteries were aged under three working conditions, i.e., CC, Pulse-100 and Pulse-2000 charging. The current pulse frequencies of 100 and 2000 Hz were selected, which were sufficiently different to facilitate the investigation of the detailed effects of current pulse frequency on the cycling performance, while staying in the high-frequency range that influences all the involved electrochemical processes (interface charge transport, charge transfer, and ion diffusion) during battery charge and discharge. The length of relaxation period was the same as current pulse, resulting in a Duty Ratio of 50% under PC charging. The average current for all three charging modes were kept the same (1C, i.e., 2.2 A), thus the current during PC charging (2C, i.e., 4.4 A) was twice as large as that during CC charging. For aging test, the batteries were discharged to a cut-off voltage of 2.5 V at a CC of 2 C (4.4 A) and charged to 4.2 V at a selected charging mode, and no constant voltage segment or relaxation period was included. After every 100 cycles, battery aging was interrupted to perform a reference performance test (RPT) for diagnosis of the battery health state.

RPT test procedures: As summarized in Table 2, before cycling and after aging for every 100 cycles, RPT tests were performed to diagnose the battery health state in a 25 °C climate chamber. The RPT consists of a capacity test and an EIS test. For the capacity test, the batteries were charged with a constant current-constant voltage (CC-CV) protocol until the current reduced to <0.11 A at the 4.2 V CV stage, then were relaxed for an hour, followed by CC discharging to 2.5 V and an hour relaxation. The charging and the discharging processes were carried out once at 0.25, 0.5, and 1 C, respectively. EIS test was performed after the capacity test, for which the batteries were first fully charged (100% SoC) with a CC-CV charging

Table 1. Battery Aging Protocols.

	CC	Pulse-100	Pulse-2000
Temperature		35 °C	
Voltage range		2.5–4.2 V	
Charging protocol	CC (2.2 A)	CC (4.4 A)	CC (4.4 A)
Discharging protocol		CC (4.4 A)	
Duty Ratio	100%	50%	50%
Periodic aging		100 charge-discharge cycles x 10	

Table 2. Reference Performance Test (RPT) Protocols.

	CC	Pulse-100	Pulse-2000
Temperature		25 °C	
Voltage range		2.5–4.2 V	
Charging protocol	CC-CV (2.2 A–4.2 V, cutoff current I < 0.11 A)		
Discharging protocol		CC (2.2 A)	
EIS tests		90%, 70%, 50%, 30%, and 10% SOC	
		6.5 kHz–10 mHz	

protocol at a current of 1 C and then discharged to 90%, 70%, 50%, 30%, and 10% SoCs then EIS tests were performed at these SoCs using a Digatron potentiostat. The frequency range of EIS was between 6.5 kHz and 10 mHz.

Operando Characterization: *Operando Raman spectroscopy:* Operando Raman spectroscopy was conducted using a Renishaw QONTOR instrument with a 532 nm laser. Electrochemical tests were performed with an operando cell and a BioLogic SP 150 potentiostat. Due to the limited frequency range of the BioLogic potentiostat, the current pulse frequency of PC charging during operando Raman measurements was set to 250 Hz (instead of 2000 Hz that was used in the battery aging test). The applied current was 0.01 C, and the discharge cut-off voltage was 0.003 V. The operando cell was ECC-Opto-Std type (EL-Cell GmbH, Hamburg, Germany). In the operando Raman test, a small (12×4 mm rectangle) piece of graphite electrode served as the working electrode, while a Li sheet acted as the counter electrode, and the electrolyte used in the experiment was composed of 1 mol of LiPF₆ dissolved in 1 L of solvent with a ratio of ethylene carbonate (EC) to diethyl carbonate (DEC) and Dimethyl Carbonate (DMC) at 1:1:1.

Operando electrochemical dilatometry: Operando electrochemical dilatometry was employed to test the thickness of negative electrode during battery cycling. The applied current was 0.2 C. The operando cell is ECC-Opto-Std type (EL-Cell GmbH, Hamburg, Germany). 10 mm diameter graphite electrode served as the working electrode, while Li disc acted as the counter electrode, and the electrolyte used in the experiment was composed of 1 mol of LiPF₆ dissolved in 1 L of solvent with a ratio of ethylene carbonate (EC) to diethyl carbonate (DEC) and Dimethyl Carbonate (DMC) at 1:1:1.

Operando X-ray absorption spectroscopy (XAS): Operando XAS was performed on NMC samples at various SoCs during the first 1.5 cycles. The measurements were performed at the KMC-2 beamline of the BESSY-II synchrotron light source in Berlin, Germany. For accurate energy calibration, pure metal foil samples were measured simultaneously with each NMC sample. The pulse current was 2 C with a frequency of 250 Hz (for the same reason as indicated above). The acquired spectra from the XAS measurements underwent data processing using an Athena Software package, including background correction, normalization, k^2 -weighting, and Fourier transformation.^[59,60] The in situ cell that was lab-designed and compatible with the KMC-2 beamline was pre-prepared in an argon-filled glove-box and then attached to the KMC-2 end station. Both NMC and graphite electrodes with a diameter of 12 mm were cut from a disassembled fresh commercial battery. The electrolyte employed in the experiment consisted of 1 mol of LiPF₆ dissolved in 1 L of solvent, with a composition ratio of EC, DEC, and DMC at 1:1:1.

Post-Mortem Analysis: As part of the experimental plan and to facilitate comparison, all batteries were cycled for 1000 cycles and then were disassembled for post-mortem analyses. First, the batteries were discharged to 2.5 V by a constant current of 0.1 C using a Neware battery test station (5V12A, Neware, China). Then, the batteries were transferred to a glove box in an argon atmosphere. Secondly, the batteries were disassembled and the graphite anode and NMC532 cathode were retrieved and washed with di-ethyl carbonate (DEC) separately. Finally, the washed electrodes were dried for 48 h and sealed in bags inside the glove box prior to further physio-chemical characterization.

Ex situ synchrotron X-ray powder diffraction (XRD): Ex situ XRD measurement was performed at PETRA III (DESY, Hamburger) on the High-Resolution Powder Diffraction Beamline P02.1. The graphite powder and NMC powder collected from cycled electrodes were filled into Kapton capillaries with a diameter of 0.8 mm and tested using an X-ray equipment voltage of 300 kV.

Ex situ Raman spectroscopy: A RXN1 (Kaiser Optical systems, Inc., MI, USA) spectrometer was employed to examine the graphite electrodes. The excitation light source was a 532 nm laser with a resampling interval of 1 cm⁻¹. The aged electrodes were measured twice. The as-obtained electrodes were measured first. Afterwards, the surface films of the electrodes were scraped off with a knife and measured again to reveal the real state of graphite excluding contribution from the surface species.

SEM: A Zeiss EVO 60 field emission SEM was employed to image the morphologies of the electrodes with a voltage of 15 kV. Samples for cross-sectional imaging were obtained by carefully cutting electrodes using a sharp knife.

Depth-dependent XPS: The XPS depth profile analysis by Ar ion beam etching to reveal subsurface information of the aged graphite electrodes. A Specs XR50 with a non-monochromated Al K α ($h\nu = 1487$ eV) X-ray source and a Phobos 1501D-DLD electron detector was employed. For data analysis, the peak fitting of the XPS spectra was carried out with a CasaXPS software using a Shirley-type background, and the peak shift induced by charging effects were corrected based on C-C at 284.91 eV in the C 1s region. For quantification of the chemical substances, relative sensitivity factor (R.S.F.) was employed to correct the peak area that represents the amount of substance. The R.S.F. of C 1s, O 1s, F 1s, and Li 1s are 1, 2.93, 4.43, and 0.0568, respectively.

Transmission Electron Microscopy (TEM): TEM imaging of the graphite and NMC electrodes was performed on a Philips CM200 and a FEI Talos F200S.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords

aging mechanism, lithium-ion batteries, NMC532/graphite, operando characterization, pulse current charging

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