

Understanding the active formation of cathode-electrolyte interphase (CEI) layer with energy level band bending for lithium-ion batteries

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The cathode-electrolyte interphase (CEI) formation between the cathode and the electrolyte is a critical factor that determines the stability of lithium-ion batteries (LiBs). The CEI layer consists of various by-products (e.g., LiF, Li₂CO₃, ROLi, and ROCO₂Li (R: alkyl group)) decomposed from redox reactions between the cathode and the electrolyte, which can lead to dramatic capacity fading and stability issues. Herein, we empirically identify the energy level band bending of a Ni-rich NMC cathode (i.e., Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O₂) with the visual evidence of Li⁺ transfer from the electrode into the CEI layer (adsorbate). The negatively charged elements tend to be present at the close surface of the cathode, while the positively charged Li⁺ migrates from the cathode into the CEI layer. Hence, a downward band bending could be depicted based on the work function and the energy level difference between the Fermi level (E_F) and the valence band maximum (E_{VBM}). The energy level alignment itself is likely to be the key process that leads to the active formation of unstable CEI layers on charge-discharge.

1. Introduction

Lithium-ion batteries (LiBs) retain great interest as an energy storage system for various applications ranging from mobile devices to electric vehicles and energy storage station for solar cells.^{1–3} Over the last decade, attention has been paid to the layered transition metal oxide batteries, which can be represented by the formula of LiNi_xCo_yMn_{1-x-y}O₂ (NMC, $x > 0$ and $y > 0$), owing to their high discharge capacity (< 200 mAh/g), high energy density, and lower cost compared to conventional LiBs (e.g., LiCoO₂).^{4–6} In addition, the mixed transition metals in the cathode between Ni, Mn, and Co can provide synergic advantages over a single transition metal oxide cathode. Ni is the key element that enables the high capacity of the battery by a two-stage redox reaction between Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺.^{7,8} Co can partially contribute to the capacity achievement, but mostly it improves the rate capability of the battery.^{9,10} Also, the presence of Co³⁺ may suppress the structural distortion resulting

from the Jahn-Teller effect of Ni³⁺.^{11,12} Mn is involved with the structural and thermal stability of the NMC cathode material.^{13–15} The structural stability is likely to be improved by Mn⁴⁺, which is electrochemically inactive.^{4,16,17} Despite of those advantages, there are major drawbacks of this series of materials. For example, the NMC battery often suffers from the irreversible capacity loss during the initial cycle, and the capacity fading/voltage decay on further cycles.^{18–20} The phase transition from the layered structure (space group: $R\bar{3}m$) into spinel and NiO rock-salt structure (space group: $Fm\bar{3}m$) is considered as the dominant factor that leads to the degradation of the NMC batteries.^{19,21–23} A number of studies have shown that the degradation process occurs both at the surface and in the bulk of the cathode material.^{21,22,24} Whereas the structural transformation to spinel occurs in the whole region of the NMC particle, the formation of NiO is often discussed as a surface reconstruction process.^{22,25,26} The increase of Ni concentration to achieve high capacities can facilitate the surface reconstruction of the active material by NiO, resulting in a high interfacial resistance.^{22,25,27} It is generally accepted that the charge transfer kinetics between the cathode and the Li⁺ at the electrode-electrolyte interphase plays an important role in the battery stability and performance.^{25,28–30} One main factor that limits the charge transfer kinetics of Li⁺ is the formation of an unstable cathode-electrolyte interphase (CEI) layer during charge and discharge.^{29,31,32} Generally, a CEI layer consists of various organic and inorganic products decomposed from electrolyte and electrode such as LiF, Li₂CO₃, MnO_x, MnF_x, CoO_x, NiO, ROLi,

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and ROCO_2Li (R: alkyl group).^{27,29,33} These chemical compounds can impede Li^+ migration at the electrode-electrolyte interphase.^{27,33} Also, previous studies have reported that the NMC cathode with high Ni concentration (i.e., Ni-rich cathode) would accelerate the CEI formation because of active electrolyte oxidations by the Ni element, which in turn leads to a thicker CEI layer.^{25,33} Thus, the CEI environment is strongly associated with the Li^+ transfer kinetics on charge-discharge. A number of studies elucidated the interfacial phenomena on the basis of band bending and energy level alignment at the CEI.^{28,29,34,35} A previous study by Becker et al. highlights the need of a surface science approach to studying the interphase property based on the energy level alignment.³⁴ In that study, a formation of an electrochemical interface was examined for a LiCoO_2 (LCO) cathode in contact with diethyl carbonate (DEC), which is a solvent often employed in the battery electrolytes. A downward band bending from the cathode bulk to the surface has been identified, implying the migration of positive charges from the cathode bulk to the surface. A similar study by Hausbrand et al. also demonstrates the band bending between the LiCoO_2 (LCO) electrode and the diethyl carbonate (DEC) electrolyte.^{28,35} The transfer of Li^+ from LCO to DEC adsorbate layer is considered as the main reason for the band bending, but there has been no empirical evidence so far.^{29,34,35} The loss of Li^+ from the cathode results in a negatively charged condition close to the cathode surface. On the other side, positive charges can be migrated into the adsorbate layer crossing the interphase. It is the charge carrier concentration that determines the interface stability between the electrode and electrolyte.

The present study explores, for the first time, the energy band bending of a Ni-rich NMC electrode, i.e., $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$ (NMC532) upon cycling with the evidence of positive charge transfer (Li^+). Whereas the energy diagrams have been often examined experimentally for solar cell applications^{36,37}, few studies have investigated energy level diagrams for lithium-ion batteries. Herein, the NMC532 electrodes were cycled with different electrochemical conditions (4.3 V, 4.5 V, and 4.7 V cut-off voltages) to induce different environments of the adsorbate layer. We could successfully depict the energy level band bending at the CEI layer based on the work function and the energy level difference between the Fermi level (E_F) and the valence band maximum (E_{VBM}). Also, the evidence of the band bending by the positive charge (Li^+) transfers, which have remained as a conceptual knowledge, has been empirically identified using a positive ion detection mode (PID) method with a secondary-ion mass spectrometry (SIMS). This paper provides key insights into the formation of the unstable CEI layer with lithium compounds during charge and discharge.

2. Experimental

Electrode preparation

The $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$ electrode was synthesized by mixing the $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$ active material (MTI) with the conductive carbon (Super C65) and polyvinylidene fluoride (PVDF) binder in a N-methyl-2-pyrrolidone (NMP, Sigma

Aldrich) solvent with the weight ratio of 80:10:10 (=active material:carbon black:PVDF). This sample was labelled as NMC5. The slurry of NMC5 was added on the aluminium current collector with a doctor blade to make the electrode. An integrated dryer inside the coater (MTI) was utilized to dry the coated film at 60 °C for overnight. This film has been taken into a vacuum oven and dried at 120 °C for 12 h. The casted cathode on the Al-current collector was roll-pressed with 10 – 15 μm thickness for three times.

Cell assembling and electrochemical measurement

Cell assembling was carried out in an Ar-glove box ($\text{H}_2\text{O} < 1$ ppm and $\text{O}_2 < 1$ ppm). The NMC5 cathodes were cut into a piece of discs to 16 mm in diameter. Li metal was used as a counter electrode, and a polypropylene membrane was employed as a separator (CELGARD Inc.). A stainless-steel spacer and a steel spring were inserted to make the coin cells (CR2032). 1 M lithium hexafluorophosphate (LiPF_6) in ethylcarbonate (EC), diethylcarbonate (DC), and dimethylcarbonate (DMC) was introduced as the electrolyte (EC:DC:DMC = 1:1:1 in volume). The cell components were sealed together using a hydraulic crimping machine (MTI, MSK-110). The assembled coin cells were electrochemically cycled with the current rate of 0.4 C in the voltage range between 2.8 – 4.3 V and 2.8 – 4.7 V. As for rate capability test, the coin cells were cycled from 0.125 C to 0.25 C and to 0.4 C in the voltage range between 2.0 – 4.5 V using an 8-channel battery analyser (MTI) at room temperature. Electrochemical impedance spectroscopy (EIS, Autolab PGSTAT204 with an FRA32 module) measurement was conducted in the frequency range of 0.1 Hz to 100 kHz with an AC amplitude of 5 mV.

Electrode material characterization

The cycled coin cells were disassembled inside the Ar-glove box. The NMC5 cathodes were cleaned using a DMC solution and dried overnight in prior to the material characterization. Ultraviolet photoemission spectroscopy (UPS) was utilized to evaluate the work function changes of the electrodes and for the interphase examination. The background chamber pressure was 10^{-9} torr and the UPS calibration of the binding energy (eV) was conducted by measuring the Fermi edge ($E_F = 0$ eV) on an Ar^+ sputtered clean Au surface. The bias voltage applied to the sample was -9 V and the energy resolution is evaluated to be 0.14 eV. The photons were emitted by a Helium gas ($\text{He I}\alpha$: 21.22 eV) non-monochromated source during the UPS measurements. A scanning electron microscope (SEM, FEI Quanta 250 FEG) was employed to compare the morphology of the NMC5 cathodes. The investigation into the cathode-electrolyte interphase was carried out by an X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA) using monochromated $\text{Al K}\alpha$ (1486.6 eV) as the X-ray source. The XPS was operated with 15 kV and 150 W power under ultra-high vacuum (10^{-9} torr). The background of the measured spectra was defined by a Shirley-type function. All spectra were calibrated by C 1s (284.6 eV) as the reference. Then, the spectra were fitted with a Gaussian-Lorentzian function using CasaXPS. A positive ion detection mode (PID) was used to visualize the CEI layer of the NMC5 cathode at different cycle

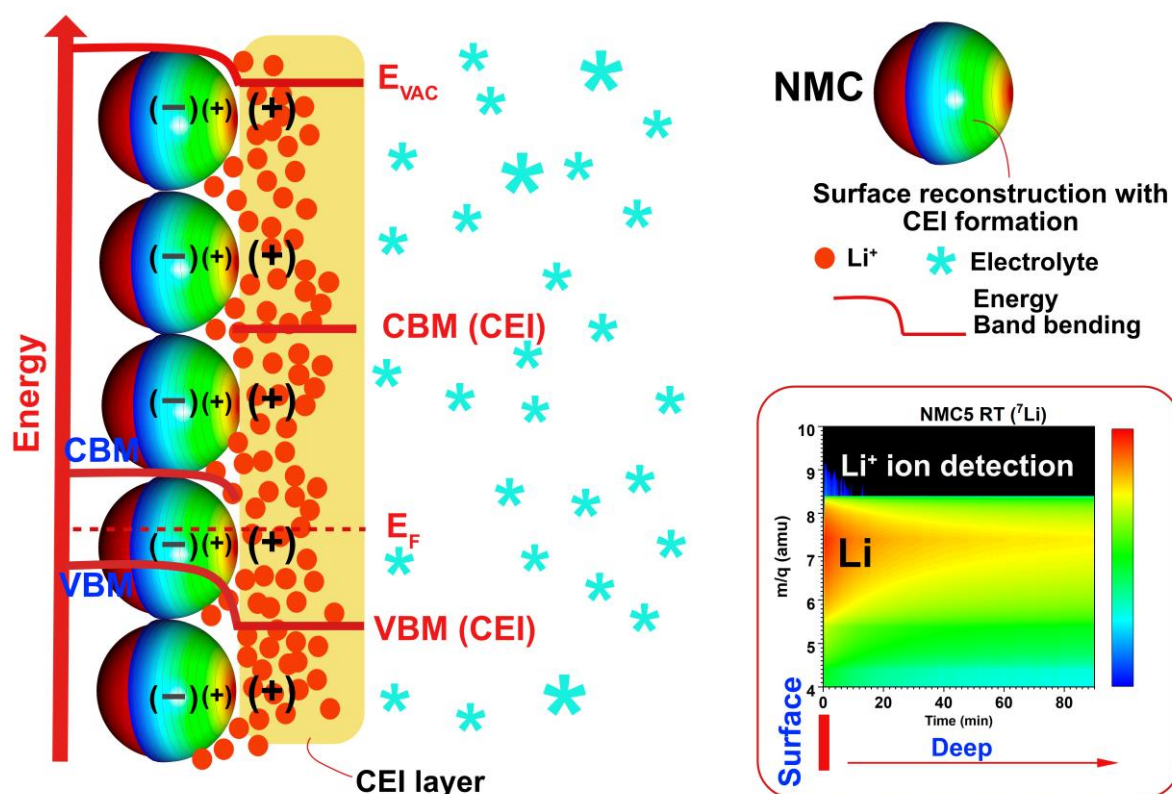


Fig. 1 Schematics of energy band bending with cathode-electrolyte interphase (CEI) layer formation and the visualization of the Li⁺ by SIMS positive ion detection mode.

condition by a SIMS (Kratos Axis ULTRA) equipped with a quadrupole mass spectrometer (HAL 7, Hidden Analytical) and an ion sputter gun (IG20, Hidden Analytical). SIMS sputtering was performed by a 1 keV Ar⁺ primary beam. The beam diameter was 100 μ m, and the applied current was 50 nA. The angle of the beam was 45° with respect to the sample surface.

3. Results and discussion

Fig. 1 reveals the schematic illustration of the energy band bending with the CEI layer, and its Li⁺ distribution visualized by the SIMS positive ion detection mode. The positive charges accumulated on the cathode surface by the Li⁺ leads to the band bending. The electrochemical behaviour of the NMC5 cells cycled with different cut-off voltages is presented in Fig. 2. To induce different CEI properties, the electrochemical cells were cycled in the voltage range of 2.8 – 4.3 V for 100 cycles, 2.8 – 4.7 V for 100 cycles and 200 cycles (Fig. 2a,b, and c). The corresponding dQ/dV plot is presented in Fig. 2d, e, and f. It is apparent that a larger voltage window and higher cycle numbers have led to significant degradation of the NMC5 cells. Also, the cell was cycled with dynamic C-rates (from 0.125 C to 0.25 C to 0.4 C, and back to 0.125 C) in the voltage range between 2.0 and 4.5 V to form an unstable CEI layer with a large amount of trapped Li⁺ (Fig. 2g). This cell has been labelled as NMC5 RT (rate capability test). The RT cycling could produce more complex and non-uniform CEI structures due to the dynamic change in the diffusion kinetics of the lithium-ions with the large

voltage gap. As a common electrochemical window for the NMC and Ni-rich NMC based batteries, a voltage range of 2.8 – 4.3 V has been chosen as a basis for the comparison purpose. To enable the full potential of the Ni-rich electrode, a high cut-off voltage is necessary. Therefore, the CEI environment is also discussed in the electrochemical window of 2.8 – 4.7 V. Furthermore, the RT cycling with the large voltage gap between 2.0 V and 4.5 V is adopted to actively induce the Li⁺ trapping in the interphase.

Fig. 3a, b reveals the work function change upon different cycled states of NMC5. The results have been obtained from the UPS measurements, and the full UPS spectra can be found in Fig. S1 – S5 (ESI†). The work function (W_F) of the NMC5 cathode at the reference state (REF) was measured to be 4.50 eV. There has been a dramatic drop in the work function to 2.84 eV after 100 cycles in the voltage range of 2.8 – 4.3 V. The work function of the NMC5 4.7V×100 and NMC5 RT was 3.59 eV and 3.57 eV, respectively, as shown in Fig. 3a, b. The decrease in the work function could be explained by the CEI formation during charge and discharge. On the other hand, the W_F of the NMC5 4.7V×200 was evaluated to be 4.48 eV, which is similar to that of the NMC5 cathode at reference state. After the long cycling, the CEI layer is likely to be decomposed and dissolved in the electrolyte, and thus exposing the inner pristine layer of the NMC5 cathode. The resistance in the electrolyte will therefore increase after 200 cycles. The EIS measurements of the NMC5 cycled for 100 and 200 cycles are compared in Fig. S6 (ESI†). The energy level difference between the Fermi level (E_F) and the

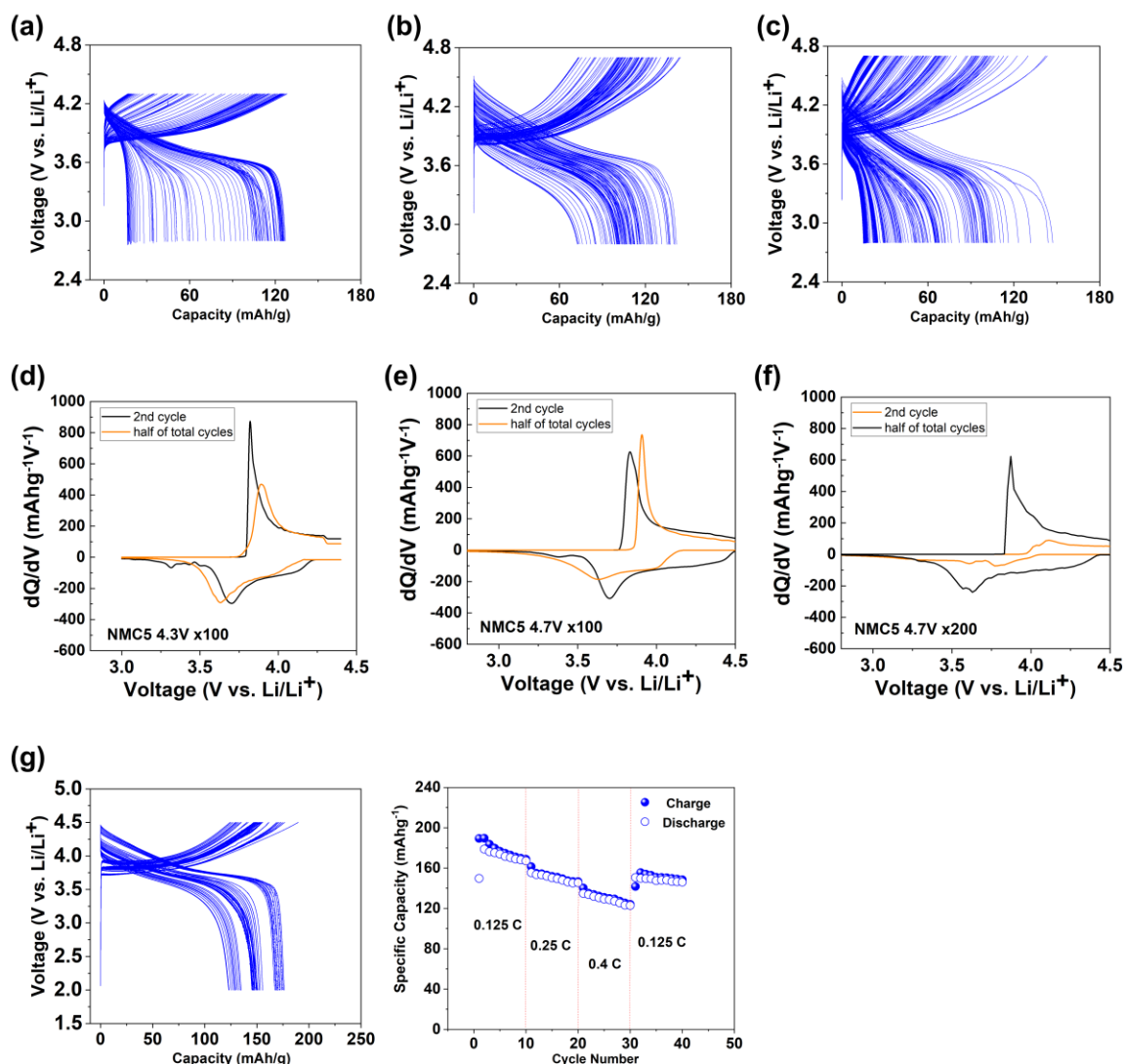


Fig. 2 Galvanostatic profiles of $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$ (NMC5) cells on different cut-off voltages at (a) 2.8 – 4.3 V for 100 cycles, (b) 2.8 – 4.7 V for 100 cycles, and (c) 2.8 – 4.7 V for 200 cycles with 0.4 C-rate current applied. The corresponded dQ/dV plots of (d) 4.3 V (100 cycles), (e) 4.7 V (100 cycles), and (f) 4.7 V (200 cycles) cut-off voltages for 2nd and half of total cycles (50th cycle or 100th cycle). (g) The rate capability cycling with 0.125 C, 0.25 C, and 0.4 C in the voltage range between 2.0 and 4.5 V.

valence band maximum (E_{VBM}) has been also evaluated (Fig. 3c, d). At reference state, the $E_{\text{F}} - E_{\text{VBM}}$ and it increased to 3.61 eV after 100 cycles in the voltage window of 2.8 – 4.3 V. The $E_{\text{F}} - E_{\text{VBM}}$ was 2.76 eV and 2.00 eV for the NMC5 4.7V \times 100 and NMC5 4.7V \times 200 samples, respectively. On the other side, this value reached 3.10 eV for the NMC5 RT cathode, which had been cycled with dynamic current rates (0.125 C \rightarrow 0.25 C \rightarrow 0.4 C \rightarrow 0.125 C). This observation will be discussed in detail in the last part of this section.

To investigate the property of the CEI layer, XPS measurements were conducted. The energy calibration was carried out based on the C 1s XPS peak at 284.6 eV. Fig. 4 compares the XPS spectra of Mn 2p, Ni 2p, and Co 2p between the cathode at reference state (REF) and the NMC5 cathode cycled for 200 cycles. The XPS binding energy of Mn ($2p_{3/2}$) and Mn ($2p_{1/2}$) were 642.6 eV and 654.1 eV, respectively, at the reference state (Fig. 4c). According to the fitting of Mn 2p, Mn^{4+} appears to be the dominant oxidation. This implies the existence

of some Mn^{3+} at the NMC5 reference. The results of the Mn oxidation states corroborate with previous studies.^{38,39} After the electrochemical cycles, the signal of Mn 2p became weaker, suggesting the dissolution of Mn in the electrolyte. One pair of spin-orbit doublet Ni ($2p_{3/2}$) and Ni ($2p_{1/2}$) peaks were observed at 854.9 eV and 872.7 eV, respectively, followed by the shake-up peaks at 860.7 eV and 879.2 eV at the reference state as can be seen in Fig. 4d. This result signifies that Ni would exist as Ni^{2+} .^{33,40} There have been also minor peaks at 856.2 eV ($2p_{3/2}$), and 874.7 eV ($2p_{1/2}$), suggesting the presence of Ni^{3+} , and corresponding shake-up peaks at 863.0 eV and 872.9 eV. Hence, Ni would be present as a mixed oxidation state between Ni^{2+} and Ni^{3+} at REF. The mixed states are often explained by the electron transfer between Mn^{4+} and Ni.^{22,40} After cycling, there has been a distinct change in the Ni 2p region. A sharp peak could be observed between 858 eV and 859 eV. This spectral change is likely to be attributed to the surface reconstruction by NiO .^{22,25} The sharp peak could be also connected to the F(KLL) transition,

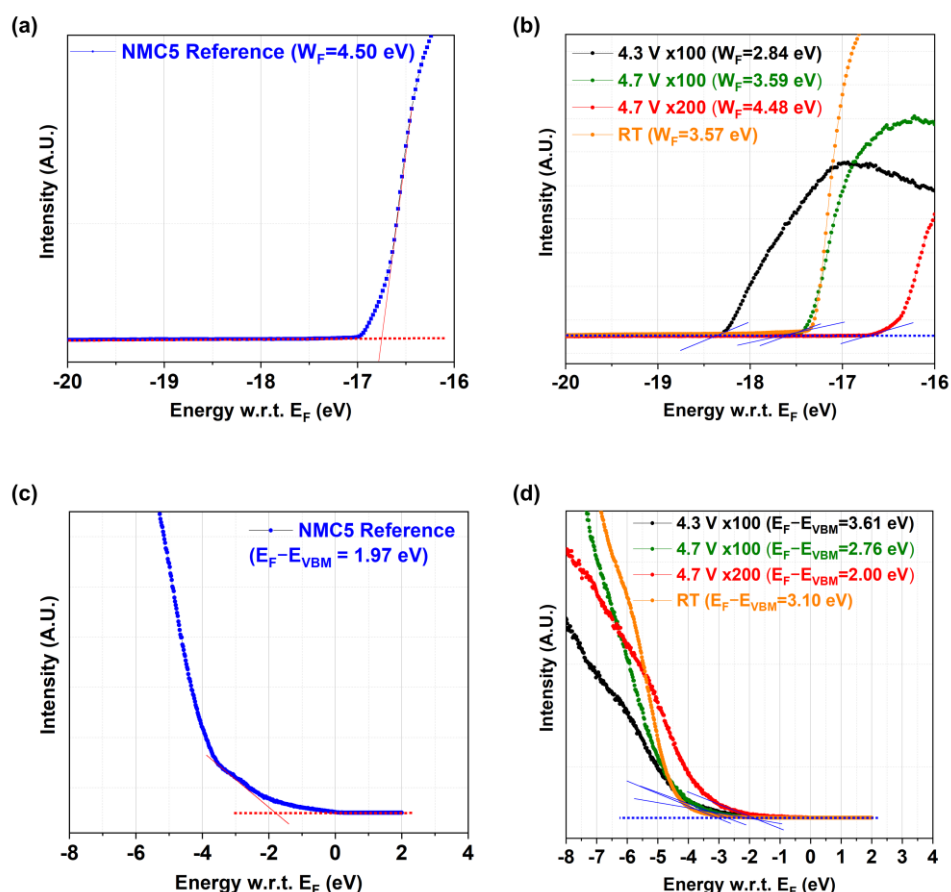


Fig. 3 Determination of work function (W_F) based on the ultraviolet photoemission spectroscopy (UPS) results on (a) NMC5 at reference state (REF), and (b) NMC5 after 100 cycles in the voltage range of 2.8 – 4.3 V and 2.8 – 4.7 V with 0.4 C current applied, after 200 cycles in the voltage range of 2.8 – 4.7 V, and after 40 cycles with dynamic current rates from 0.125 C to 0.25 C to 0.4 C and back to 0.125 C in the voltage range of 2.0 – 4.5 V. Determination of VBM ($=E_F - E_{VBM}$) from the ultraviolet photoemission spectroscopy (UPS) measurements on (c) NMC5 at reference state (REF), and (d) NMC5 after 100 cycles in the voltage range of 2.8 – 4.3 V and 2.8 – 4.7 V with 0.4 C current applied, after 200 cycles in the voltage range of 2.8 – 4.7 V, and after 40 cycles with dynamic current rates from 0.125 C to 0.25 C to 0.4 C and back to 0.125 C in the voltage range of 2.0 – 4.5 V.

which can be assigned to a CEI species such as NiF_2 (857.8 eV).^{25,41} The XPS spectra of Co 2p are presented in Fig. 4e. The Co ($2p_{3/2}$) and Co ($2p_{1/2}$) peaks were found at 780.2 eV and 795.9 eV, respectively, suggesting the major presence of Co^{3+} at reference state. A broad satellite peak could be also observed at approximately 785.0 eV, signifying the existence of a small amount of Co^{2+} .^{17,42} However, after 200 cycles, the Co 2p peak nearly disappeared. Similar to Mn 2p, this implies the dissolution of Co in the electrolyte.

The XPS spectra at C 1s, O 1s, F 1s and Li 1s are shown in Fig. 5. Three C 1s peaks could be found at 284.6 eV, 285.9 eV, and 290.0 eV for the reference sample (REF) as can be seen in Fig. 5a. The peak at 284.6 eV is attributed to the conductive carbon, while the peaks at 285.9 eV, and 290.0 eV are associated with the PVDF binder. After the electrochemical cycles, the PVDF binder underwent some changes. The C 1s spectrum at the reference state differs from that of the cycled state. The conductive carbon possibly reacted with the electrolyte forming a CEI layer. Such layer can further evolve during charge and discharge, resulting in a passive layer that impedes Li^+ migration. The O 1s spectra is shown in Fig. 5b. There have been two major

peaks at 529.9 eV and 531.9 eV, which can be assigned to the lattice oxygen and the metal carbonate/ Li_2CO_3 peaks, respectively, for the reference sample (Fig. 5b). After cycling, a spectral shift towards a higher energy could be observed. This change is likely to be ascribed to the formation of NiO on the active material surface and/or the dissolution of the transition metal oxides into the electrolyte.^{18,22,29} The XPS F 1s spectrum is presented in Fig. 5c. Contrary to expectations, the change in the F 1s spectrum was insignificant after cycling. LiF , Li_xPF_y , and $Li_xPO_yF_z$ are the main components that are supposed to be identified in the F 1s spectra as the decomposed electrolyte species.^{43,44} In addition, NiF_2 , CoF_2 , and MnF_2 have been also expected as CEI species, which can contribute to the F 1s spectra.^{29,45,46} The absence of those contributions could be explained by the dissolution of the thick CEI layer after long and aggressive cycling for 200 cycles (~4.7 V). The CEI seems to be decomposed and dissolved in the electrolyte, exposing the pristine layer located underneath the CEI layer. This result is in line with that of the UPS analyses and the XPS spectra obtained from the transition metals. Fig. 5d exhibits the XPS spectra of Li 1s. At the reference state, a major peak can be found at 55.9 eV.

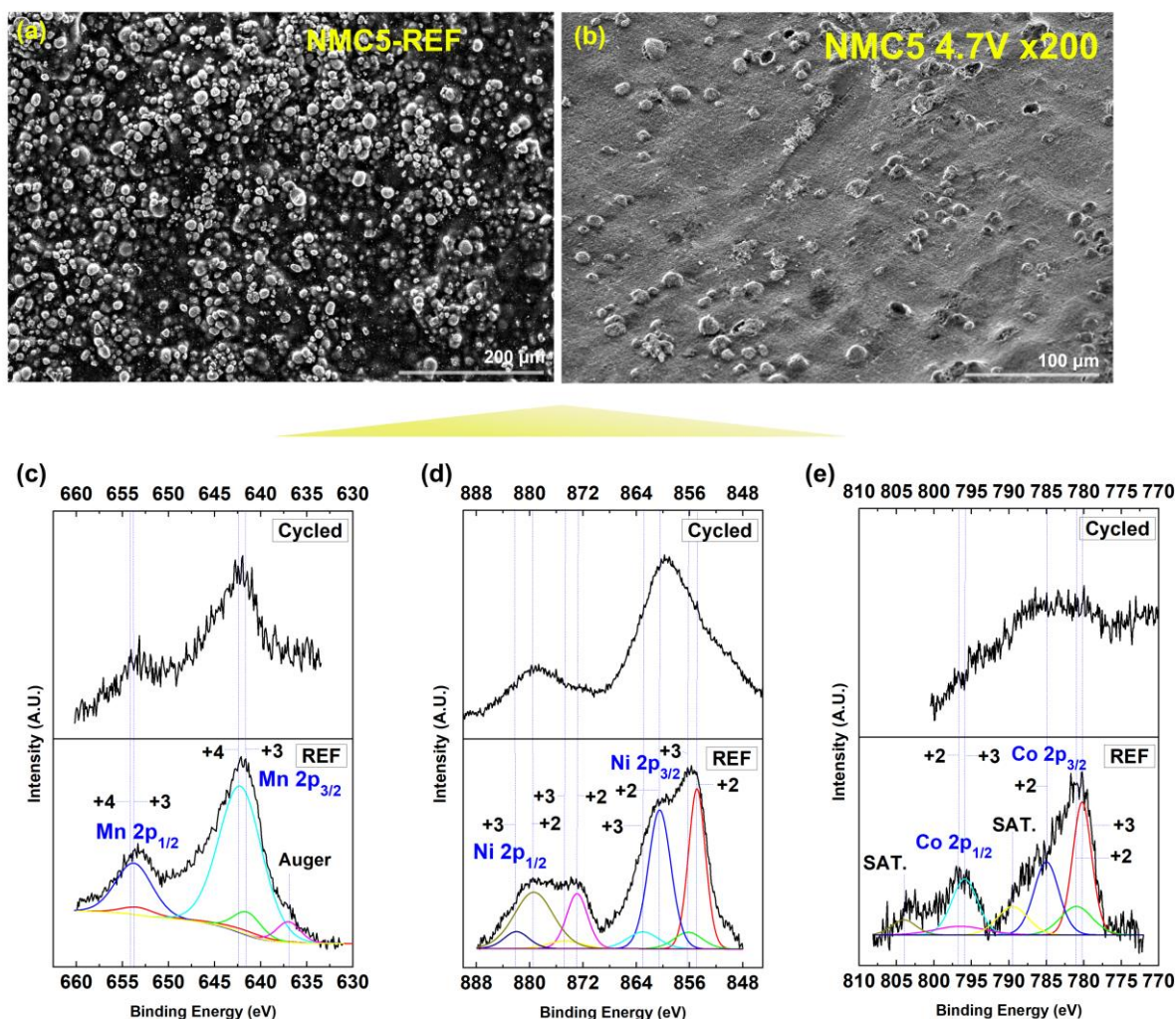
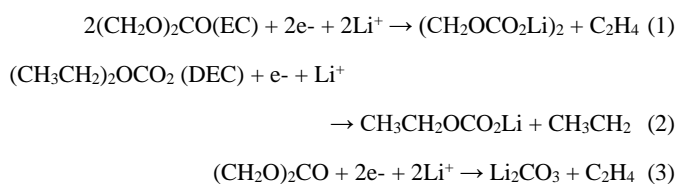


Fig. 4 SEM observations on (a) NMC5 at reference state (REF) and (b) NMC5 after 200 cycles (Cycled) in the voltage range of 2.8–4.7 V with 0.4 C current applied. The corresponding surface analyses by XPS between NMC5 (REF) and NMC5 (Cycled) at (c) Mn 2p, (d) Ni 2p, and (e) Co 2p. The label SAT. indicates a satellite peak.

This peak can be ascribed to a metallic lithium, but this peak nearly disappeared after 200 cycles.

A positive-ion detection mode has been adopted based on the SIMS depth profiling. This method enables the visualization of the major species that constitute the CEI layer as can be seen in Fig. 6. The visualization approach offers the key information on the stability of the CEI layer. At the reference state, ^{60}Ni , ^{59}Co , ^{58}Ni , and ^{55}Mn have been identified on the cathode surface (Fig. 6a). The initial loss of Li^+ upon first cycle is presented in Fig. S7 (ESI †), and the visualization of the accumulated CEI layer on top of the pristine cathode is exhibited in Fig. S8 (ESI †). After 200 cycles, various elemental bands occurred, implying the increase in the number of the CEI species as presented in Fig. 6b. In general, the chemical reaction between the electrolyte and the Li^+ can produce the Li_2CO_3 , Li_2O , and LiF components.^{27,33} The atomic mass units (amu) of ~ 26.0 and ~ 30.0 possibly correspond to the LiF and Li_2O , respectively. ^{12}C and ^7Li were also notable, but the colour and the brightness have been somewhat weakened as compared to the elemental bands at reference state (NMC5-REF). This indicates some dissolution of the CEI species into the

electrolyte, and is in agreement with the UPS result of the NMC5 4.7V \times 200 sample. Also, the XPS results (Cycled) support the decomposition of the CEI layer. There have been also some bands between 50.0 and 60.0 amu. This observation signifies the CEI components stemming from the transition metals such as NiO , MnO_n , CoO_n , NiF_2 , NiF_3 , MnF_2 , LiF_2 , and CoF_3 .^{29,41,47,48} As an alternative cycle condition (RT cycled), the cathode was cycled with dynamic current rates between 0.125 C, 0.25 C, and 0.4 C for 40 cycles to induce the CEI formation with minimum dissolution into the electrolyte. In addition, this approach appears to be helpful in trapping Li^+ in the interphase (Fig. 6c), which can be explained by the electron reduction process as follows⁴⁹:



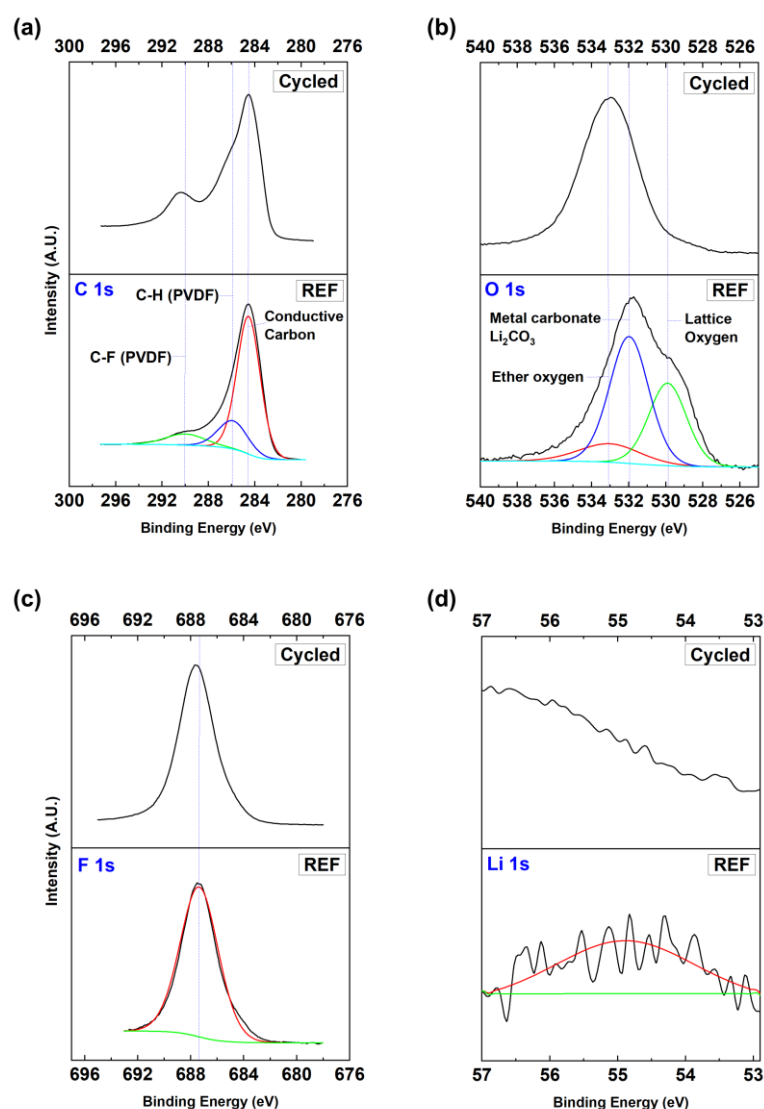


Fig. 5 Comparison of XPS analyses between NMC5 (REF) at reference state and NMC5 (Cycled) after 200 cycles in the voltage range of 2.8 – 4.7 V with 0.4C current applied. The collected XPS spectra at (a) C 1s, (b) O 1s, (c) F 1s, and (d) Li 1s.

The Li^+ trapping mechanism can also involve an electro-catalytical process with the transition metals.⁵⁰ We could successfully depict the energy level diagram of the $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$ cathode upon different cycled states on the basis of the work functions and the $E_{\text{F}} - E_{\text{VBM}}$ evaluations (Fig. 7). The work function and $E_{\text{F}} - E_{\text{VBM}}$ at the different cycle conditions have been compared in Fig. 7a. The energy band structure was described based on the corresponding visualization of the amount of lithium-ions trapped in the interphase. The band structure may slightly vary upon precise (electro)chemical environments during cycling. As mentioned earlier, the work function (W_{F}) of NMC5 at reference state was measured to be 4.5 eV, and it dramatically dropped to 2.84 eV when the battery was cycled for 100 cycles up to 4.3 V. As a consequence, a distinct band bending could be observed as exhibited in Fig. 7c. It is known that the energy level position and band bending can determine the charge transfer barriers at the interphase.³⁵ The band bending shows a downward trend from the cathode bulk to

the surface. This finding suggests a positive charge transfer from the cathode bulk to the surface layer. The loss of Li^+ from the battery cathode leads to the negatively charged cathode vacancies close to the surface, whereas the positive charges, i.e., Li^+ can be present across the junction between the pristine NMC5 and the CEI layer.^{34,35} The irreversible Li^+ loss with the formation of vacancies is a common phenomenon leading to the capacity fading and voltage decay during cycling, which has been reported by several previous studies.^{51,52} The migration of such Li^+ could be attributed to the chemical potential difference between the pristine NMC5 cathode and the newly formed CEI layer.^{28,35} Normally, the CEI layer includes lithium compounds formed during the redox reactions between the electrode and the electrolyte. However, the concentration of Li^+ from such lithium components in the CEI layer is likely to be very low as compared to that of the cathode bulk, and thus causes the chemical potential difference. On the other hand, W_{F} increased after 100 cycles up to 4.7 V and it became 3.59 eV. As mentioned before, the CEI

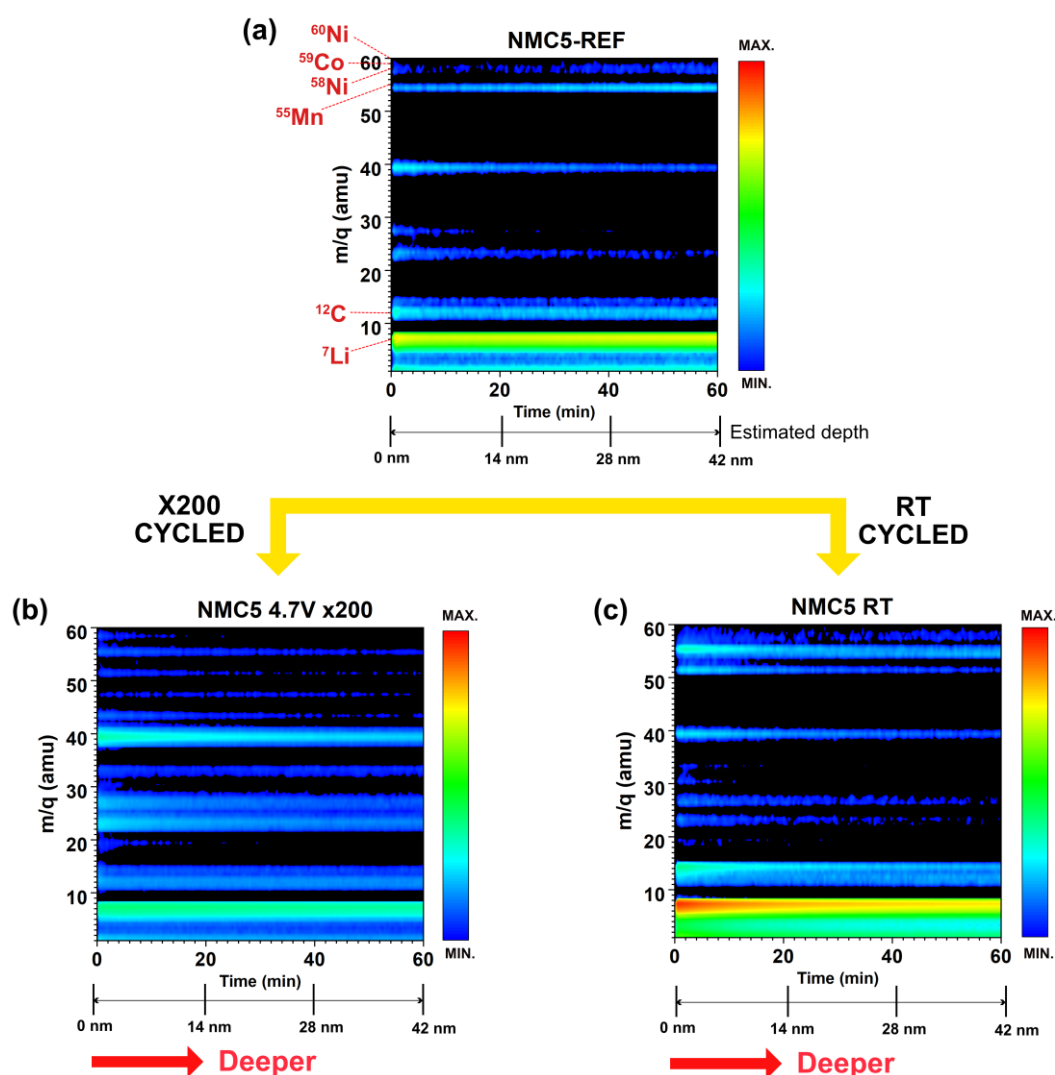


Fig. 6 Visualization of the cathode-electrolyte interphase (CEI) formation by SIMS positive-ion detection (PID) mode with estimated depth on (a) NMC5 (REF) at reference state, (b) NMC5 after 200 cycles in the voltage range of 2.8 – 4.7 V with 0.4C current applied, and (c) NMC5 after 40 cycles with dynamic current rates from 0.125 C to 0.25 C to 0.4 C and back to 0.125 C in the voltage range of 2.0 – 4.5 V.

layer continued to undergo decomposition into the electrolyte, which in turn can expose the inner layer of the NMC5 cathode. This reaction could be considered as a redox reaction that involves electrons transfer. Consequently, the downward band bending by the positive charges has disappeared. However, the exposed inner layer is not identical to the pristine material (NMC5-REF). A detailed look into the ^7Li band confirms a slight decrease in the concentration of Li^+ in the pristine material after 200 cycles (Fig. 7d). The $E_F - E_{\text{VBM}}$ was approximately 2.0 eV for the NMC5 4.7V \times 200 cathode, while it was evaluated to be 1.97 eV for the pristine cathode. Also, W_F slightly increased to 4.48 eV, and thereby the major downward band bending disappeared. Instead, there has been a slight downward band bending. Hence, the difference in the amount of Li^+ between the bulk layer and the CEI layer seems to be very small. With the RT cycled layer, we could induce a Li^+ trapped or accumulated CEI layer as displayed in Fig. 7e. The process of the Li^+ trapping

can be described by equation (1), (2), and (3). The dynamic interactions between the electrode and the electrolyte have produced sets of Li^+ compounds such as Li_2O , Li_2CO_3 , LiF , $\text{R}(\text{OCO}_2\text{Li})_2$ where R is an organic group, Li_xPF_y , and $\text{Li}_x\text{PO}_y\text{F}_z$. These compounds can act as a physical barrier for the Li^+ diffusion during charge and discharge. In addition, the formation of the Li^+ compounds signify irreversible loss of a certain amount of Li^+ from the pristine cathode (bulk), which can result in a notable capacity fading. Taken together, the concentration of negatively charged elements (e.g., Li^+ vacancies) tends to rise at the close surface of the NMC5, whereas the positively charged Li^+ migrates from the cathode into the adsorbate (i.e., CEI layer) possibly due to the difference in the chemical potential of lithium. Therefore, at the junction of cathode/CEI layer, a depletion region occurs similar to a semiconductor application. As a result, a downward band bending could be observed in the energy band diagram of the RT cycled sample (Fig. 7e). During the energy

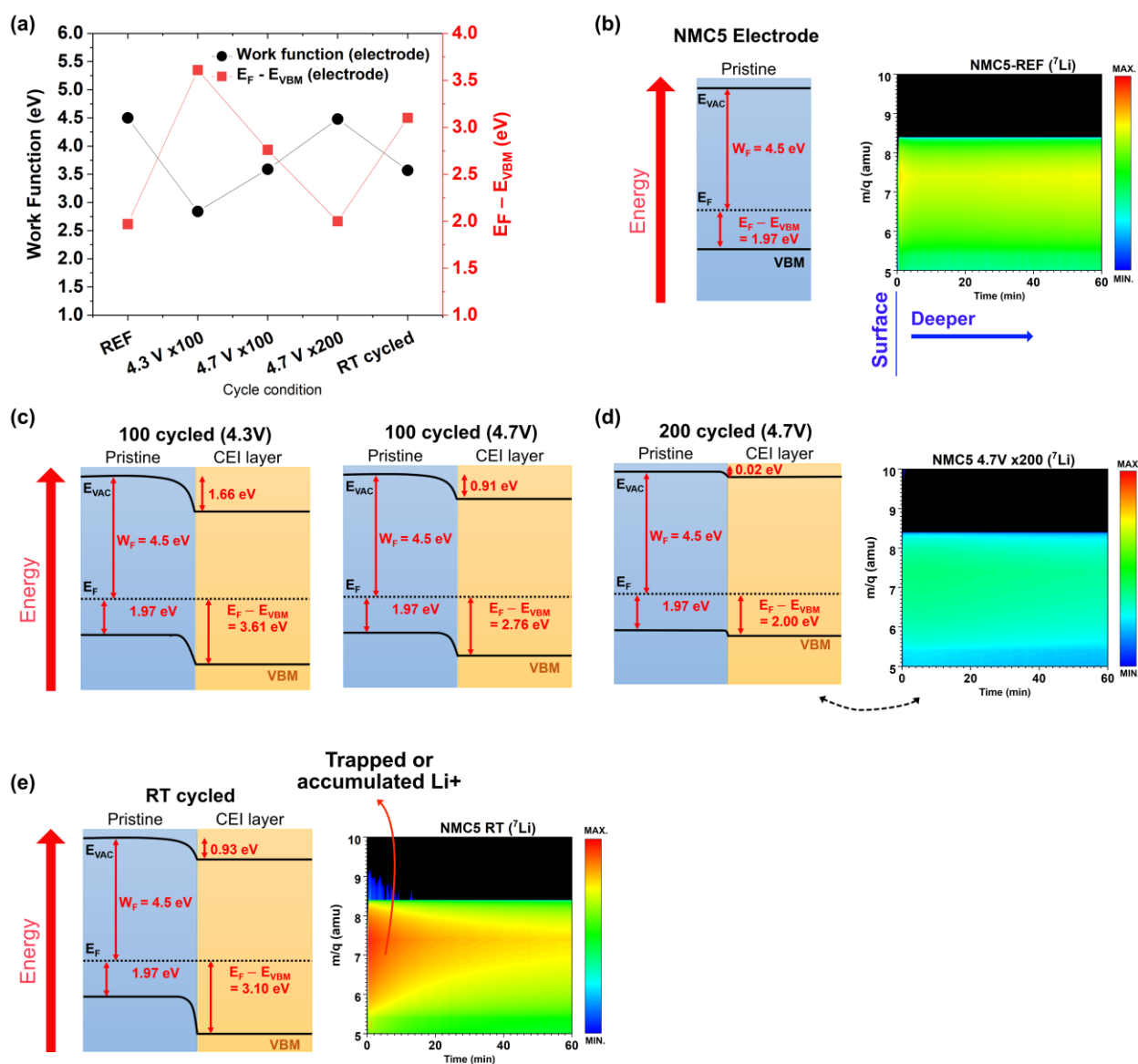


Fig. 7 (a) Work function and $E_F - E_{VBM}$ upon different cycled states of the NMC5 cathode. Energy level diagram of the (b) NMC5 at reference state (REF) with the visualization of ^7Li distribution, (c) NMC5/CEI after 100 cycles in the voltage range of 2.8 – 4.3 V and 2.8 – 4.7 V, and (d) after 200 cycles in the voltage range between 2.8 V and 4.7 V (at 0.4 C-rate) with the visualization of ^7Li distribution, and (e) NMC5 after 40 cycles with dynamic current rates from 0.125 C to 0.25 C to 0.4 C and back to 0.125 C (voltage range: 2.0 – 4.5 V) with the visualization of the trapped ^7Li .

level alignment with the band bending, electrons from the conduction band of the CEI layer diffuse to the conduction band of the cathode. This process may promote the redox reactions between the CEI and the electrolyte because of the charge concentration change, causing performance decay of the lithium-ion battery.

4. Conclusions

The present study has experimentally identified the band bending in the energy level diagram of a Ni-rich NMC electrode upon cycling with the visual evidence of Li^+ migration from the pristine material into the adsorbate, i.e., the CEI layer. The irreversible loss of Li^+ from the cathode at the early stage of cycling may cause the Li^+ migration at the junction of

cathode/CEI layer. When the lithium-ions migrated, vacancies can be equally formed. These vacancies can serve as the negative charges, which continuously form close to the cathode surface. During further electrochemical cycles, the deintercalated Li^+ are likely to be accumulated in the CEI layer, and thus leading to the notable band bending, facilitating the charge concentration change. This process will accelerate the formation of the unstable CEI layer and will be eventually dissolved in the electrolyte, causing severe capacity decay of the lithium-ion battery. The downward band bending by the migration of positive charges (Li^+) into the CEI layer has been empirically proved. This study will shed some light on the development of Ni-rich cathode with enhanced stability for high-capacity lithium-ion batteries.

Author contributions

Y.B.Q. conceived the idea and supervised the research. T.K. conceived the idea, and conducted experiments and analyses. L.K.O. contributed to part of the experiments. All authors contributed to writing the paper.

Conflict of interest

There are no conflicts to declare.

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Notes and references

- 1 M. Armand and J. M. Tarascon, *Nature*, 2008, **451**, 652–657.
- 2 D. Larcher and J.-M. Tarascon, *Nat. Chem.*, 2015, **7**, 19–29.
- 3 T. Kim, W. Song, D. Y. Son, L. K. Ono and Y. Qi, *J. Mater. Chem. A*, 2019, **7**, 2942–2964.
- 4 A. Manthiram, J. C. Knight, S. T. Myung, S. M. Oh and Y. K. Sun, *Adv. Energy Mater.*, 2016, **6**, 1501010.
- 5 N. Nitta, F. Wu, J. T. Lee and G. Yushin, *Mater. Today*, 2014, **18**, 252–264.
- 6 W. Lee, S. Muhammad, T. Kim, H. Kim, E. Lee, M. Jeong, S. Son, J. H. Ryou and W. S. Yoon, *Adv. Energy Mater.*, , DOI:10.1002/aenm.201701788.
- 7 M. Dixit, M. Kosa, O. S. Lavi, B. Markovsky, D. Aurbach and D. T. Major, *Phys. Chem. Chem. Phys.*, 2016, **18**, 6799–812.
- 8 K. Luo, M. R. Roberts, R. Hao, N. Guerrini, D. M. Pickup, Y.-S. Liu, K. Edström, J. Guo, A. V. Chadwick, L. C. Duda and P. G. Bruce, *Nat. Chem.*, 2016, **8**, 1–17.
- 9 Z. Li, N. a. Chernova, M. Roppolo, S. Upreti, C. Petersburg, F. M. Alamgir and M. S. Whittingham, *J. Electrochem. Soc.*, 2011, **158**, A516.
- 10 S.-H. Kang, P. Kempgens, S. Greenbaum, a. J. Kropf, K. Amine and M. M. Thackeray, *J. Mater. Chem.*, 2007, **17**, 2069.
- 11 A. N. Mansour, L. Croguennec and C. Delmas, *Electrochem. Solid-State Lett.*, 2005, **8**, A544.
- 12 J. R. Croy, M. Balasubramanian, D. Kim, S.-H. Kang and M. M. Thackeray, *Chem. Mater.*, 2011, **23**, 5415–5424.
- 13 S. M. Bak, E. Hu, Y. Zhou, X. Yu, S. D. Senanayake, S. J. Cho, K. B. Kim, K. Y. Chung, X. Q. Yang and K. W. Nam, *ACS Appl. Mater. Interfaces*, 2014, **6**, 22594–22601.
- 14 D. Y. W. Yu and K. Yanagida, *J. Electrochem. Soc.*, 2011, **158**, A1015.
- 15 S.-T. Myung, F. Maglia, K.-J. Park, C. S. Yoon, P. Lamp, S.-J. Kim and Y.-K. Sun, *ACS Energy Lett.*, 2017, **2**, 196–223.
- 16 S.-T. Myung, K.-S. Lee, Y.-K. Sun and H. Yashiro, *J. Power Sources*, 2011, **196**, 7039–7043.
- 17 L. Li, L. Wang, X. Zhang, M. Xie, F. Wu and R. Chen, *ACS Appl. Mater. Interfaces*, 2015, **7**, 21939–21947.
- 18 J. P. Pender, G. Jha, D. H. Youn, J. M. Ziegler, I. Andoni, E. J. Choi, A. Heller, B. S. Dunn, P. S. Weiss, R. M. Penner and C. B. Mullins, *ACS Nano*, 2020, **14**, 1243–1295.
- 19 T. Li, X. Z. Yuan, L. Zhang, D. Song, K. Shi and C. Bock, *Electrochem. Energy Rev.*, 2020, **3**, 43–80.
- 20 M. D. Radin, S. Hy, M. Sina, C. Fang, H. Liu, J. Vinckeviciute, M. Zhang, M. S. Whittingham, Y. S. Meng and A. Van der Ven, *Adv. Energy Mater.*, 2017, **7**, 1602888.
- 21 W. Liu, P. Oh, X. Liu, M.-J. Lee, W. Cho, S. Chae, Y. Kim and J. Cho, *Angew. Chemie Int. Ed.*, 2015, **54**, 4440–4457.
- 22 S.-K. Jung, H. Gwon, J. Hong, K.-Y. Park, D.-H. Seo, H. Kim, J. Hyun, W. Yang and K. Kang, *Adv. Energy Mater.*, 2014, **4**, 1300787.
- 23 A. Manthiram, *Nat. Commun.*, 2020, **11**, 1–9.
- 24 S. Hwang, W. Chang, S. M. Kim, D. Su, D. H. Kim, J. Y. Lee, K. Y. Chung and E. a Stach, *Chem. Mater.*, 2014, **26**, 1084–1092.
- 25 W. Li, A. Dolocan, P. Oh, H. Celio, S. Park, J. Cho and A. Manthiram, *Nat. Commun.*, 2017, **8**, 14589.
- 26 W. Zhao, J. Zheng, L. Zou, H. Jia, B. Liu, H. Wang, M. H. Engelhard, C. Wang, W. Xu, Y. Yang and J. G. Zhang, *Adv. Energy Mater.*, 2018, **8**, 1–9.
- 27 M. Gauthier, T. J. Carney, A. Grimaud, L. Giordano, N. Pour, H.-H. Chang, D. P. Fenning, S. F. Lux, O. Paschos, C. Bauer, F. Maglia, S. Lupart, P. Lamp and Y. Shao-Horn, *J. Phys. Chem. Lett.*, 2015, **6**, 4653–4672.
- 28 R. Hausbrand, G. Cherkashinin, H. Ehrenberg, M. Gröting, K. Albe, C. Hess and W. Jaegermann, *Mater. Sci. Eng. B*, 2015, **192**, 3–25.
- 29 G. Cherkashinin, M. Motzko, N. Schulz, T. Späth and W. Jaegermann, *Chem. Mater.*, 2015, **27**, 2875–2887.
- 30 M. Weiss, F. J. Simon, M. R. Busche, T. Nakamura, D. Schröder, F. H. Richter and J. Janek, *Electrochem. Energy Rev.*, 2020, **3**, 221–238.
- 31 T. R. Jow, S. A. Delp, J. L. Allen, J.-P. Jones and M. C. Smart, *J. Electrochem. Soc.*, 2018, **165**, A361–A367.
- 32 P. M. Chekushkin, I. S. Merenkov, V. S. Smirnov, S. A. Kislenco and V. A. Nikitina, *Electrochim. Acta*, 2021, **372**, 137843.
- 33 I. Takahashi, H. Kiuchi, A. Ohma, T. Fukunaga and E. Matsubara, *J. Phys. Chem. C*, 2020, **124**, 9243–9248.
- 34 D. Becker, G. Cherkashinin, R. Hausbrand and W. Jaegermann, *J. Phys. Chem. C*, 2014, **118**, 962–967.
- 35 R. Hausbrand, D. Becker and W. Jaegermann, *Prog. Solid State Chem.*, 2014, **42**, 175–183.
- 36 L. Qiu, S. He, L. K. Ono and Y. Qi, *Adv. Energy Mater.*, 2020, **10**, 1902726.
- 37 S. Wang, T. Sakurai, W. Wen and Y. Qi, *Adv. Mater. Interfaces*, 2018, 1800260.
- 38 J. Zhi, S. Li, M. Han, Y. Lou and P. Chen, *Adv. Energy Mater.*, 2018, **8**, 1–11.
- 39 Y. Li, L. Cui, C. Tan, X. Fan, Q. Pan, Y. Chu, S. Hu, F. Zheng, H. Wang and Q. Li, *Chem. Eng. J.*, 2022, **430**, 132985.

- 40 D. Kim, J. M. Lim, Y. G. Lim, J. S. Yu, M. S. Park, M. Cho and K. Cho, *Chem. Mater.*, 2015, **27**, 6450–6456.
- 41 Y. M. Lee, K. M. Nam, E. H. Hwang, Y. G. Kwon, D. H. Kang, S. S. Kim and S. W. Song, *J. Phys. Chem. C*, 2014, **118**, 10631–10639.
- 42 J. Yuan, J. Wen, J. Zhang, D. Chen and D. Zhang, *Electrochim. Acta*, 2017, **230**, 116–122.
- 43 T. Eriksson, A. M. Andersson, C. Gejke, T. Gustafsson and J. O. Thomas, *Langmuir*, 2002, **18**, 3609–3619.
- 44 K. Edstr, T. Gustafsson and J. O. Thomas, *Electrochim. Acta*, 2004, **50**, 397–403.
- 45 D. T. Nguyen, J. Kang, K. M. Nam, Y. Paik and S. W. Song, *J. Power Sources*, 2016, **303**, 150–158.
- 46 N. Tran, L. Croguennec, M. Ménétrier, F. Weill, P. Biensan, C. Jordy and C. Delmas, *Chem. Mater.*, 2008, **20**, 4815–4825.
- 47 M. Noh and J. Cho, *J. Electrochem. Soc.*, 2013, **160**, A105–A111.
- 48 T. Eriksson, A. M. Andersson, A. G. Bishop, C. Gejke, T. Gustafsson and J. O. Thomas, *J. Electrochem. Soc.*, 2002, **149**, A69.
- 49 A. M. Andersson, D. P. Abraham, R. Haasch, S. MacLaren, J. Liu and K. Amine, *J. Electrochem. Soc.*, 2002, **149**, A1358.
- 50 J. A. Gilbert, I. A. Shkrob and D. P. Abraham, *J. Electrochem. Soc.*, 2017, **164**, A389–A399.
- 51 W. Hua, B. Schwarz, R. Azmi, M. Müller, M. S. Dewi Darma, M. Knapp, A. Senyshyn, M. Heere, A. Missyul, L. Simonelli, J. R. Binder, S. Indris and H. Ehrenberg, *Nano Energy*, 2020, **78**, 105231.
- 52 D. Mohanty and H. Gabrisch, *J. Power Sources*, 2012, **220**, 405–412.

Table of Contents (TOC)

The downward band bending induced by the migration of positive charges (Li^+) into the cathode-electrolyte interphase (CEI) layer after electrochemical cycling.

