Multi-length-scale x-ray spectroscopies for determination of surface reactivity at high voltages of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ vs $\text{Li}_4\text{Ti}_5\text{O}_{12}$

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ABSTRACT

The surface evolution of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) electrodes cycled in a carbonate-based electrolyte was systematically investigated using the high lateral resolution and surface sensitivity of x-ray photoemission electron microscopy combined with x-ray absorption spectroscopy and x-ray photoelectron spectroscopy. On the cathode, we attest that the surface of the pristine particles is composed of adventitious Li_2CO_3 together with reduced Ni and Co in a +2 oxidation state, which is directly responsible for the overpotential observed during the first de-lithiation. This layer decomposes at 3.8 V vs Li^+/Li , leaving behind a fresh surface with Ni and Co in a +3 oxidation state. The charge compensation upon Li^+ extraction takes place above 4.0 V and is assigned to the oxidation of both Ni and oxygen, while Co remains in a +3 oxidation state during the whole redox process. We also identified the formation of an inactive surface layer already at 4.3 V, rich in reduced Ni and depleted in oxygen. However, at 4.9 V, NiO-like species are detected accompanied with reduced Co. Despite the highly oxidative potential, the surface of the cathode after long cycling is free of oxidized solvent byproducts but contains traces of LiPF_6 byproducts (LiF and PO_xF_y). On the LTO counter electrode, transition metals are detected only after long cycling vs NCA to 4.9 V as well as PVdF and LiPF_6 byproducts originating from the cathode. Finally, harvested cycled electrodes prove that the influence of the crosstalk on the electrochemical performance of LTO is limited.

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I. INTRODUCTION

The continuously growing demand for high energy density Li-ion batteries to power long-mileage electric vehicles or to be used as backup-power connected to smart grids is leading a large research effort toward the choice of suitable cathode active materials.^{1–3} Layered oxides are considered appropriate materials due to their high specific charge, low volume changes, and high operating voltage vs Li^+/Li .^{1,4} Among these promising cathode materials, some are already commercially available for automotive applications, such as $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA).¹ Despite the high theoretical specific charge of NCA (279 mAh/g), its practical specific charge is limited to about 200 mAh/g due to the restriction to cycling below 4.2 V vs Li^+/Li ^{5,6} to avoid the drastic capacity fading

observed when cycling up to higher potentials at both room and high temperatures.⁷ Previous scientific reports have tried to explain the degradation mechanisms by investigating the surface and the bulk of the NCA particles. It was suggested that the capacity fading and the concomitant impedance rise⁸ are related to various possible reactions such as (i) electrolyte oxidation leading to the deposition of a resistive surface layer composed of organic–inorganic electrolyte byproduct species,⁹ (ii) surface structural changes and formation of an electrochemically inactive NiO-like phase,^{10,11} (iii) structural defects such as cation mixing that impedes Li-ion diffusion,^{12,13} and (iv) microstructural changes such as cracking and electrical isolation of active particles.^{14,15} The question of electrolyte stability at high potentials and the oxidation mechanism are still not fully elucidated, as reflected in the

contradictory results reported for the surface reactivity.^{16,17} In this respect, it is worth mentioning that the calculated highest occupied molecular orbital (HOMO) levels of most solvents and salts used in the electrolyte are above 6 V vs Li^+/Li ,¹⁸ making them theoretically stable against electrochemical oxidation when used with layered oxide cathodes. The surface structural change at high voltages is reported to be caused by Li-ion extraction and/or oxygen loss from the surface, accompanied with the presence of reduced transition metals (TMs) at high oxidative voltages.¹⁹ Unlike other layered high voltage cathode materials, such as many lithium nickel–manganese–cobalt oxide ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, NMC) materials, the oxygen release from NCA upon cycling is minimal and it could only be identified recently by using high sensitive on-line electrochemical mass spectrometry (OEMS).^{17,20} The oxygen release from NCA starting at 4.17 V has been associated with the oxidation of oxygen after the complete oxidation of Ni. However, a significant amount of CO_2 gas is also observed to be continuously released during charge and discharge at the early stages of cycling. This behavior is explained by the oxidation of an adventitious Li_2CO_3 layer²¹ and its possible reformation during discharge.¹⁷

In this context, and given the importance of the surface reactivity on the battery performance, we are revisiting in this study the surface evolution of the NCA electrode cycled vs $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as a counter electrode. For this purpose, we employ x-ray photoemission electron microscopy (XPEEM) as a unique tool to investigate the chemical surface evolution on individual particles of commercial-like Li-ion electrodes.²² Spatially-resolved XPEEM measurements are combined with x-ray absorption spectroscopy (XAS) acquired in total electron yield (TEY) and total fluorescence yield (TFY) modes, allowing us to perform depth profile analysis from the surface to the bulk of the particles. X-ray photoelectron spectroscopy (XPS) is also employed to complement the XAS measurements. To improve the fundamental understanding of the various reactions taking place at the surface of the NCA electrodes and at its interface with the electrolyte, post mortem measurements are performed on NCA electrodes cycled at room temperature and extracted at different potentiostatic steps during the first cycle and after long cycling. The surface of the LTO counter electrode is also investigated to elucidate any possible “crosstalk” of species between the cathode and the anode. The use of LTO as the counter electrode is essential to track the possible migration/diffusion of organic and/or inorganic species formed at the surface of the cathode in the case of electrolyte oxidation, as was proposed on similar cathode materials.^{23–25}

With this approach, we first shed light on the reaction mechanism of the adventitious Li_2CO_3 , its evolution upon cycling, and its impact on the electrochemical cycling behavior. Second, we identify the TMs’ oxidation state upon cycling at the surface and deeper in the bulk of the NCA particles, as well as the contribution of the oxygen in the charge compensation at high voltages. Third, we clarify the effect of the high potential on the oxidation of the electrolyte and the stability of the binder. Fourth, we address the possible dissolution of TMs and organic–inorganic species into the electrolyte at high voltages and their migration/diffusion to the counter electrode. Fifth, we elucidate the detrimental effects of all the surface reactions on the overall electrochemical cell performance.

II. EXPERIMENTAL METHODS AND TECHNIQUES

A. Electrode preparation

Cathode and anode electrodes were prepared by mixing, respectively, the active material powders $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA, Toyota) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO, Süd Chemie) with conductive carbon (Super-C 65, Imerys) and polyvinylidene fluoride (PVdF, Arkema Kynar HSV 900), in a ratio of 80:10:10 wt. %. Both active materials were stored outside the glovebox under atmospheric conditions. *N*-methyl-2-pyrrolidone (NMP, Alfa Aesar) was used as a solvent to prepare homogeneous slurries, which were cast on Al foil and dried under dynamic vacuum at 80 °C overnight. Electrodes with a diameter of 13 mm were obtained by punching the dried coatings. A further heating at 120 °C under dynamic vacuum was performed to remove the remaining water before inserting the electrodes in an Ar-filled glovebox. The particle size and the surface morphology of the electrodes were evaluated by scanning electron microscopy (SEM), as showed in [supplementary material](#), Fig. S1. The NCA powder is composed of primary and secondary particles, in the range of $\sim 1\ \mu\text{m}$ and $\sim 15\ \mu\text{m}$, respectively, while LTO is composed of single particles of $\sim 2\ \mu\text{m}$ in size. The electrodes investigated by XPEEM were pressed at 2 tons prior to cycling in order to reduce their surface roughness and porosity, a step required for obtaining good XPEEM contrast images with a high resolution ([supplementary material](#), Fig. S1).²² Binder-free electrodes have also been prepared for the XPS measurements by pressing the mixture composed of 65% active material and 35% Super-C on the Al current collector, allowing a straightforward analysis of the contribution of the binder stability at high voltages upon cycling via comparative experiments excluding fluorine contributions arising from PVdF.

B. Electrochemical characterization

Cells for the post mortem analyses were assembled using LP30 electrolyte [1M LiPF_6 in 1:1 w/w ethylene carbonate (EC) and dimethyl carbonate (DMC), Gotion] and using a glass fiber separator inserted between two Celgard 2400 separators, to avoid silicate contamination at the surface of the electrodes. A cell in a 3-electrode configuration, using metallic Li as the reference and cycled on a VMP3 (BioLogic) system, was used in order to ensure a correct weight balancing ratio between NCA and LTO and to allow an accurate recording of the potential of both the positive and the negative electrodes [Fig. 1(a)]. The cells containing the electrodes for the post mortem measurements were assembled in a 2-electrode configuration and cycled using a BAT-SMALL system (Astrol Electronic). The full-cell cycling was performed in a constant current mode between 3.0 V and 4.9 V (all potentials mentioned here are referenced to the Li^+/Li potential) at room temperature, by applying a C/10 cycling rate, assuming a theoretical specific charge of 280 mAh/g for NCA and 175 mAh/g for LTO. The electrode balancing of the full cells was $\sim 1.0:2.4$ in mass (NCA/LTO), considering a specific charge of 280 mAh/g (first charge) and 175 mAh/g for NCA and LTO, respectively. The loading of the active material was $\sim 0.7\ \text{mg}/\text{cm}^2$ for the NCA electrode and $\sim 1.7\ \text{mg}/\text{cm}^2$ for the LTO electrode, respectively. LC30 electrolyte, consisting of 1M LiClO_4 salt in a mixture of 1:1 w/w of EC and DMC, was used in some instances as a fluorine-free electrolyte for the analysis of the binder stability at high voltages to

FIG. 1. (a) Galvanostatic cycling performed in a 3-electrode cell using NCA as a working electrode, LTO as a counter electrode, and Li as a reference, in LP30 electrolyte within the potential window 3.0–4.9 V vs Li^+/Li . (b) Long-term cycling performance of the half and full cells cycled between 3.0 V and 4.9 V.

exclude the fluorine contribution from the LiPF_6 salt. The cells were stopped at different cutoff potentials and disassembled in an Ar-filled glovebox. The extracted electrodes were rinsed with DMC to remove the residual salt and EC from the surface and then mounted on suitable sample holders for post mortem analyses. The transfer between the glovebox and the analysis instruments was performed in specially designed transfer chambers to prevent exposure of the samples to air.

C. Post mortem XPEEM measurements

The XPEEM measurements have been performed at the Surfaces/Interfaces Microscopy (SIM) beamline at the Swiss Light Source (SLS), Switzerland. Spectromicroscopy measurements were performed by measuring the secondary electrons locally emitted from the sample under ultra-high vacuum (UHV) condition (base pressure 5×10^{-10} mbar) at room temperature. Elemental contrast images are obtained by pixel-wise division of two images recorded at the respective x-ray absorption edge and pre-edge (see Table S1). XAS spectra were obtained by recording a sequence of XPEEM images as a function of photon energy using linearly polarized light. All the spectra were normalized by the incoming flux measured on a gold mesh, except for the C K-edge spectra which were normalized using the signal from gold microparticles deposited on a pristine electrode.²² For the energy scale, we used the nominal energy values measured in one of the measurement runs; for measurements carried out during other beamtimes, the energy scale was aligned using the C K-edge π^* bonds at 285.5 eV and the Ni L-edge located at 853.5 eV associated with the Ni^{2+} main component. XPEEM has an excellent lateral resolution better than 70 nm, allowing us to perform simultaneously surface microscopy and spectroscopy at the level of single particles.²⁶ The limited escape depth of electrons from materials, in the range of 2–3 nm for low energy electrons, makes XPEEM very surface sensitive and, therefore, particularly well suited for the study of surfaces and interfaces in Li-ion batteries.

D. Post mortem XAS measurements

The acquisition of XAS spectra in total electron yield and total fluorescence yield (TEY and TFY) was carried out at the Surfaces/Interfaces Microscopy (SIM) beamline at the Swiss Light Source (SLS), Switzerland. Secondary electrons emitted by the sample as a function of photon energy are collected by measuring the electron current via a picoammeter (Keithley 6517B). Simultaneously, the x-ray fluorescence signal is collected by using a large area Si diode detector located close to the sample surface. In this way, we collect XAS spectra from approximately 10 nm and 300 nm depths from the surface for the TEY and TFY modes, respectively. Since the particle size is in the micrometer range, by combining XPEEM, TEY, and TFY detection modes, we are able to probe from the very surface to the bulk of the active material particles.

E. Post mortem XPS measurements

XPS spectroscopy measurements are performed on a VG ESCALAB 220iXL spectrometer (Thermo Fisher Scientific) with a base pressure of $\sim 2 \times 10^{-9}$ mbar using a focused monochromatized Al K_α radiation (1486.6 eV) with a beam size of $\sim 500 \mu\text{m}^2$. The spectrometer is pre-calibrated by performing a measurement on a clean silver surface, whereby the Ag $3d_{5/2}$ peak is aligned to a binding energy of 368.25 eV with a full width at half-maximum of 0.78 eV at a pass energy of 30 eV. All survey spectra are recorded with a dwell time of 50 ms, using a pass energy of 50 eV in steps of 0.5 eV. For spectra acquired in a narrow energy span, these last parameters were of 30 eV and 0.05 eV, respectively. Peak deconvolution is performed by applying the sum of Gaussian (70%) and Lorentzian (30%) line shapes after a Shirley-type background subtraction. Control spectra were recorded at the beginning and at the end of each experiment to rule out sample degradation. The binding energy scale is calibrated using the Super-C carbon 1s peak (C–C binding energy of 284.5 eV). Some of the XPS measured electrodes were binder-free. The absence of the organic binder PVdF makes it easier to deconvolute the F 1s and C 1s core levels and helps us to monitor accurately

the electrolyte decomposition for the salt LiPF_6 and the solvents EC and DMC.

III. RESULTS AND DISCUSSION

A. Electrochemical performance

Figure 1(a) shows the galvanostatic profile at room temperature acquired in a 3-electrode configuration cell using NCA as a working electrode (cathode), LTO as a counter electrode (anode), and metallic Li as a reference. The cell was cycled within the potential window of 3.0–4.9 V vs Li^+/Li and provided a specific charge at room temperature with respect to NCA of 255 mAh/g and 212 mAh/g during the first charge and discharge, respectively, with an equivalent loss of about 15%, in good agreement with previous results.¹⁴ The LTO anode is cycled along its characteristic plateau of 1.55 V vs Li^+/Li at both charge and discharge, confirming the good weight balancing between the cathode and the anode in the cell. We can also observe a substantial difference in the NCA potential profile between the first and the second charge. The galvanostatic curve displays an overpotential maximum seen as a steep potential increase during the early stages of the first charge up to 4.25 V, followed by a sharp drop to 3.7 V. Afterward, the potential progressively increases to 4.9 V. During the second charge, the overpotential disappears and the potential profile shows a monotonic increase. This behavior has been recently attributed to the decomposition of the adventitious Li_2CO_3 , based on x-ray diffraction and infrared spectroscopy measurements.²¹

The long-term cycling stability of both the half-cell NCA vs Li and the full-cell NCA vs LTO cycled between 3.0 V and 4.9 V in LP30 electrolyte at C/10 cycling rate is shown in Fig. 1(b). After 100 cycles, the half cell presents a capacity fading of ~31% with respect to the second charge, while in the full-cell configuration, the fading is more pronounced and accounts to ~42%, an equivalent of 23 mAh/g difference. As expected, cycling the cell to the upper cutoff potential of 4.3 V leads to lower capacity fading in both half- and full-cell configurations (Fig. S2, [supplementary material](#)). After 100 cycles, the capacity fading is 10% and 25% for half- and full-cell configurations, respectively.

Samples cycled to different cutoff potentials were investigated and compared with pristine electrodes and electrodes soaked in the electrolyte at open circuit potential (OCP) for 36 h. The following cathode and their respective anode counter-electrode samples were selected for the investigation of the surface evolution during cycling: (i) 3.8 V, after the overpotential step rise, (ii) 4.0 V, 4.3 V, and 4.9 V to monitor the oxidation state of the TMs and the oxygen, as well as the electrolyte oxidation, (iii) 3.0 V, at the end of discharge, where the reformation of Li_2CO_3 has been reported,¹⁷ and (iv) long-term cycling (100 cycles) with upper cutoff potentials of 4.3 V and 4.9 V to examine the impact of the high potential on the surface degradation and capacity fading.

B. Pristine NCA electrode

Elemental contrast images acquired on a NCA pristine electrode at the Ni L-edge/pre-edge, C and F K-edges/pre-edges, and at the carbonate peak are presented in [supplementary material](#), Fig. S3, showing the location of the NCA particles and conductive carbon, as well as the distribution of the PVdF binder and the carbonates on

the surface of the electrode. The combination of the single-element contrast images obtained with XPEEM provides a unique way to picture the surface of the electrode. Figure 2(a) shows the exact location of the NCA particles (blue) and conductive carbon (red), by overlapping the elemental images acquired at the Ni L-edge/pre-edge ([supplementary material](#), Fig. S3a) and the one acquired at the C K-edge/pre-edge ([supplementary material](#), Fig. S3b).

Similarly, the map in Fig. 2(b) shows the location of conductive carbon (red) and carbonate species (in yellow). It is clear that the carbonate species are found in positions complementary to the carbon areas and overlap with the position of NCA particles visible in Fig. 2(a). The carbonate derives from the exposure of the NCA powder to air and moisture.^{17,21,27–30} The PVdF binder is also observed to follow the outline of the NCA particles [green areas in Fig. 2(c)], suggesting a preferential coverage of the active material. The local XAS C K-edge spectrum acquired on conductive carbon [red spectrum in Fig. 2(d)] shows the π^* and σ^* features at 285.5 eV and 292 eV, respectively, typical for carbon bonds, whereas the spectrum acquired on the NCA particle shows intense peaks associated with the presence of Li-alkyl carbonate and Li_2CO_3 at 288.6 eV and 290.4 eV, respectively. Furthermore, looking at the XPEEM XAS spectra at the Ni and Co L-edges acquired on the NCA particles [Figs. 2(e) and 2(f)], both elements are found in a reduced state on the surface, assigned to the +2 oxidation state.³¹ This is in contrast with the Ni and Co L-edge spectra acquired in TEY and TFY modes, where the signal from the +3 oxidation state dominates, as expected for both Co and Ni in pristine NCA, with only a small feature below 780 eV still visible in the Co L-edge in the TEY and TFY from Co^{2+} .³² This result shows that the surface of the NCA particles underwent a strong change caused either by intermixing of the surface cations with the carbonate layer and/or by the variation in Li and oxygen, both consumed by the formation of the Li_2CO_3 layer.^{12,27,30} The XPEEM O K-edge acquired on pristine NCA particles ([supplementary material](#), Fig. S4) shows the absence of the component at 528.8 eV on the surface attributed to the electron transition from the 1 s state to the hybridized O 2p- $\text{Ni}^{3+/4+}$ 3d orbitals, typical of layered structures, which is instead present deeper in the particles, i.e., as detected in XAS in both TEY and TFY modes. However, on the surface, we observe a component at about 532 eV originating from electron transition from the 1 s state to the hybridized O 2p- Ni^{2+} 3d orbitals, such as in the NiO-like cubic phase,³³ and another component at about 534 eV, associated with the Li_2CO_3 phase.³⁴ The XPEEM O K-edge spectrum supports our observation that the surface, within the depth detection limit of approximately 2–3 nm, contains negligible NCA in a layered oxide form, consisting instead mainly of carbonate species and reduced Ni and Co.

The XPS measurements performed on pristine binder-free NCA electrodes and acquired on C 1s, O 1s, Ni 2p, and Co 2p, presented in [supplementary material](#), Fig. S5, probe an area of ~0.2 mm² of the sample. While it is difficult to identify the component related to the Li_2CO_3 from the C 1s core level spectrum because of its low intensity, the presence of Li_2CO_3 covering the surface of pristine NCA can be ascertained by looking at the O 1s. Two main components are detected in the O 1s spectrum located at 528.7 eV and 531.5 eV, originating from the NCA layered oxide and the adventitious species, respectively. The absence of the Co 2p_{3/2} signal at 779.8 eV and the weak signal of the Ni 2p_{3/2} at ~855.4 eV are in line

FIG. 2. Reconstructed elemental mapping of the NCA pristine electrode showing (a) the NCA particles (blue) and the conductive carbon areas (red); (b) the conductive carbon areas (red) and the presence of carbonates (yellow); (c) the NCA particles (blue), conductive carbon areas (red), and binder position (green). (d) Local C K-edge spectra acquired on individual carbon and NCA particles. XPEEM XAS spectra acquired at (e) Ni and (f) Co L-edges compared to XAS performed in TEY and TFY modes.

with XPEEM results and confirm that the NCA particles are covered with a carbonate layer that attenuates the TM signal from the layered oxide.

C. NCA surface evolution at early stages and after long cycling

1. Overpotential at the first charge

In Fig. 3, we show the local XAS spectra acquired on individual particles of the NCA electrodes cycled at room temperature in LP30 electrolyte at the Ni, Co L-edges and O, C K-edges. The spectra of the pristine NCA electrode are compared to those of the electrode at open circuit potential (i.e., when the electrode was kept in contact with the electrolyte for 36 h) and at different potentiostatic steps during the first cycle [Fig. 1(a)]. At OCP, no obvious changes are observed in the C K-edge, while slight changes are observed in the Co L-edge and O K-edge, indicated by a low attenuation of the Co^{2+} components associated most likely with the (partial) dissolution of

the reduced TMs. This observation confirms that the carbonate layer containing reduced Ni and Co is stable in contact with the electrolyte up to 36 h. When the cell is stopped at 3.8 V, just after the overpotential step rise, the carbonate, Ni^{2+} , and Co^{2+} components on the NCA particles disappear [Figs. 3(d), 3(a), and 3(b), respectively]. Both Ni and Co are in the oxidized +3 state as expected for pristine NCA.

The O K-edge XAS spectrum changes as well [Fig. 3(c)], with the clear appearance of a peak at 528.8 eV attributed to the electron transition from the O 1s state to the hybridized O 2p-Ni^{3+/4+} 3d orbital, typical of the NCA layered oxide. Moreover, the peak at about 534 eV, attributed to the presence of carbonate species, disappears. These results demonstrate that the Li_2CO_3 layer decomposes electrochemically at the early stage of cycling, while the reduced Ni and Co species revert to the expected bulk oxidation state (+3) (or eventually dissolve into the electrolyte). Moreover, by correlating the NCA surface chemistry with the electrochemical behavior, we demonstrate that the overpotential observed at

FIG. 3. XPEEM XAS spectra of NCA particles at different potentiostatic steps, acquired at the (a) Ni and (b) Co L-edges and (c) O and (d) C K-edges. (e) The C K-edge acquired on conductive carbon areas.

the beginning of the first de-lithiation (oxidation) is caused by the aged layer on NCA and is found to vanish after the first cycle [Fig. 1(a)].

The XPS measurements shown in [supplementary material](#), Fig. S5, are in line with the XPEEM XAS results. After full lithiation at 4.9 V and full de-lithiation at 3.0 V, the signals of both Ni 2p and Co 2p are visible and intense with respect to the pristine state, confirming again the removal of the carbonate layer from the surface. In an attempt to elucidate the contribution of the carbonate layer covering the NCA particles to the overall specific charge during the first de-lithiation, we estimated the maximum specific charge that 3 nm of Li_2CO_3 , NiCO_3 , and CoCO_3 could provide. The details of the calculation are presented in Note 1, [supplementary material](#), showing a maximum contribution of 1% with respect to the NCA theoretical specific charge. Thus, the irreversible oxidation of the carbonate layer does not explain the 15% irreversibility in specific charge observed during the first cycle [Fig. 1(a)].

2. Cationic and anionic redox processes

The charge compensation upon Li-ion extraction and insertion from and into the NCA structure is investigated by monitoring the oxidation states of the Ni and Co from the L-edge spectra and the O from the K-edge spectra presented in Figs. 3(a)–3(c). As a first approximation, from the XPEEM contrast images, we take the average oxidation of the different particles as a representative of the whole electrode. The progressive increase of the Ni oxidation from Ni^{3+} at 3.8 V and 4.0 V to Ni^{4+} at 4.3 V [Fig. 3(a)] indicates that the charge compensation happens mainly on the Ni and not on the Co atoms, since the latter shows no spectral changes between 3.8 V and 4.9 V, but just a slight shift of 0.4 eV to higher photon energy [Fig. 3(b)]. The shift observed on the Co L-edge is attributed to the change in the local environment around the Co atoms due to the Li^+ removal, Ni oxidation, and O oxidation.^{32,35} The typical Co oxidation from +3 to +4 during Li-ion de-intercalation would have manifested as a peak shift to a higher photon energy (+0.8 eV)

FIG. 4. Reconstructed XPEEM chemical maps of the NCA electrodes stopped at (a) 4.3 V, (b) 4.9 V, (c) 3.0 V, and (d) after long-term cycling at 4.9 V. The gray color corresponds to carbon particles taken at the C K-edge (285.5 eV), whereas red and blue correspond to the NCA particles. The blue particles show a higher oxidation state, calculated by dividing the maximum intensity of the Ni L-edge component at 855.8 eV ($\text{Ni}^{3+/4+}$) by the component at 853.4 eV (Ni^{2+}). From the elemental contrast images, we extracted Ni, Co L-edges, and O K-edge spectra from three different areas representing the most reduced (min, in red), intermediate oxidized (avg, in blue), and highly oxidized (max, in black) Ni.

accompanied with a peak broadening toward the higher energy region and an intensity drop of the main peak.^{36,37} However, from 4.3 V to 4.9 V, no further change is observed in the average oxidation of Ni. It is also worth mentioning that Ni at the surface is not fully oxidized to +4, since the component at 853.5 eV associated with the Ni²⁺ is still visible. Such a behavior is explained by the formation of an inactive layer at the surface of NCA most likely related to the partial loss of oxygen.³⁸ The electrode stopped at 3.0 V at the end of the re-lithiation shows that the redox process of the active surface is reversible, since the Ni⁴⁺ is reduced back to Ni³⁺.

Interestingly, the analysis of the O K-edge spectra [Fig. 3(c)] reveals a significant contribution of the O 2p band to the redox mechanism. It is evidenced by the appearance of the component at 531 eV at 4.3 V, which remains visible at 4.9 V. This component is reversible and disappears at the end of lithiation at 3.0 V. A similar observation was reported recently^{39–43} where the O K-edge is used to track the “O-redox” activity in the bulk of the oxide particles by monitoring the evolution of the component at 530.8 eV. Such an observation is more straightforward when using transmission XAS methods that probe the bulk of the material. In our study, it is the first time that we observe the anionic redox process at the surface (within 3 nm depth) of high voltage cathode materials. We can detect the surface oxygen activity because NCA presents very low oxygen release rate at high potentials, ~700 times less compared to Li-rich NMC, for example.^{20,44} The contribution of the oxygen to the charge compensation is also confirmed for the second cycle, as shown by the re-appearance of the component at 530.8 eV in the O K-edge (Fig. S6 in the [supplementary material](#)).

As mentioned above, the spectra presented in Fig. 3 represent an average of the different NCA particles. However, thanks to the XPEEM excellent lateral resolution and its imaging capability, a statistics study has been performed on multiple NCA particles to provide a realistic distribution of the cationic and anionic redox processes. The elemental contrast images presented in Fig. 4 are obtained on electrodes cycled up to 4.3 V, 4.9 V, and 3.0 V during the first cycle and after long-term cycling to 4.9 V and show the Ni oxidation state distribution at the surface of the different NCA particles, where blue particles are more oxidized (toward +4) and red particles are more reduced (+2/+3). We can note from the color code that at 4.3 V and 4.9 V, the NCA particles are not homogeneously oxidized, while at 3.0 V, after full lithiation, the particles are all in a +3 oxidation state. From the elemental contrast images, we extracted the Ni and Co L-edges and the O K-edge spectra from three different areas having mostly reduced (min), intermediate oxidized (avg), and highly oxidized (max) Ni, as shown in Fig. 4. At 4.3 V, independent of the Ni oxidation state, the Co features do not show any changes confirming again that Co does not take part in the redox process. However, in the O K-edge (Fig. 4), the component located at 531 eV associated with oxygen oxidation is only present for the particles with intermediate and highly oxidized Ni and not in the particles with reduced Ni. At 4.9 V, the oxygen spectra show a similar behavior for the intermediate and highly oxidized Ni, but for the reduced Ni, the oxygen shows additional components located at 532 eV associated with NiO-like species. The particles containing reduced Ni show reduced features also in the Co L-edge, as a shoulder increase at low photon energy related to reduced Co in the +2 oxidation state. At 3.0 V, after full lithiation, as expected, the component related to the oxidized oxygen disappears for most of

the particles, while on the highly reduced particles, the presence of the NiO-like species is still observed on the surface. The surface evolution of the NCA is correlated directly with the amount of oxygen evolving at the different states of charge and the oxidation state of the NCA particles. The ratio of the O to the sum of the TMs (Ni + Co), presented in [supplementary material](#), Fig. S7, shows a clear signal intensity drop in the oxygen ratio for the reduced NCA particles at 4.3 V and 4.9 V, confirming that the reduced Ni and Co are related to the oxygen loss from the surface. For the oxidized particles, the oxygen loss is less significant and the ratio remains relatively constant. Such an observation suggests the following surface mechanism concerning the oxygen activity at high potential. (i) Formation of a very thin oxygen-depleted layer, underneath which the O is redox active; the thickness of the oxygen-depleted layer is not homogeneously distributed across the particles and is voltage dependent. (ii) NiO-like species are mainly formed at 4.9 V. After long-term cycling stopped at 4.9 V, the trend remains the same; however, the Ni is less oxidized, and the components associated with oxidized oxygen and the NiO-like species are no longer visible. Our findings bring new insight into the accepted knowledge for the charge compensation,^{17,32,33,45} by suggesting that the oxidation of both Ni and oxygen above 4 V plays a united role in the charge compensation, while Co is passive since it remains in a +3 state during the whole redox process. We also demonstrate the formation of an inactive surface layer already at 4.3 V, rich in reduced Ni and depleted in oxygen. However, at 4.9 V, NiO-like species are detected together with reduced Co.

3. Ni oxidation gradient from the surface to the bulk

Depth profiling information can be obtained by comparing the XPEEM data, which probe the first 3 nm of the surface, with XAS spectra acquired in TEY and TFY modes, which probe down to 10 nm and 100 nm, respectively. The Ni and Co L-edge XAS-TFY measurements presented in Fig. 5 are collected on NCA electrodes cycled during de-lithiation to 4.3 V and 4.9 V and to a fully lithiated state at 3.0 V. It is clear from the Ni L-edge TFY spectra that most of the Ni in the bulk of NCA particles are oxidized to the +4 state at 4.3 V, and the remaining fraction is oxidized at 4.9 V. This process is reversible after the lithiation at 3.0 V, where Ni is reduced back to the +3 state. At the region near the surface, the Ni L-edge TEY spectra are in line with the above XPEEM measurements, confirming that Ni is not fully oxidized to the +4 state at both 4.3 V and 4.9 V. Surprisingly, at 4.3 V, the Ni is much more reduced with respect to 4.9 V. This behavior is explained by the strong dissolution of the reduced TMs at 4.9 V, leading to a thinning of the oxygen-depleted surface layer. The strong dissolution of the TMs at 4.9 V will be addressed further in Sec. III D 2.

4. Side reactions at high potentials: Electrolyte instability

The possible formation of an organic and an inorganic surface layer on the NCA and conductive carbon particles is investigated for the cathode in fully de-lithiated and lithiated states at 4.9 V and 3.0 V, respectively, as well as after long-term cycling. The stability of both solvents (EC, DMC) and salt (LiPF₆) is examined by combining (i) C 1s, F 1s, and P 2p XPS core level measurements and (ii) XPEEM measurements with local XAS on C

FIG. 5. Ni and Co L-edge XAS spectra acquired in TFY [(a) and (b)] and TEY [(c) and (d)] modes on NCA electrodes cycled up to 4.3 V, 4.9 V, and after lithiation to 3.0 V.

and F K-edges acquired separately on NCA and conductive carbon particles.

In Fig. 6, we show the results of XPS measurements performed on pristine and cycled NCA binder-free electrodes in LP30 electrolyte. The use of binder-free electrodes simplifies the interpretation and deconvolution of the C 1s and F 1s peaks by avoiding the overlapping signals from the PVdF. The absence of changes in the C 1s core level [Fig. 6(a)] during cycling demonstrates that organic species related to the EC and DMC oxidized byproducts are deposited neither on the surface of the NCA nor on conductive carbon particles. The XPEEM measurements on the C K-edge presented in Figs. 3(d) and 3(e) acquired locally on the NCA and conductive carbon, respectively, support the XPS observations. Indeed, in the C K-edge spectra, there is no evidence for solvent-based oxidized byproducts covering the NCA or the carbon particles, as suggested by the absence of peaks at 288.6 eV and 290.4 eV, attributed to alkyl carbonates and lithium carbonate, which are typical electrolyte oxidation byproducts.⁴⁶ At the end of the lithiation at 3.0 V, the C K-edge also reveals no reformation of carbonate species on the surface of the electrode, in contrast to previous reports.^{16,17}

FIG. 6. (a) C 1s, (b) F 1s, and (c) P 2p XPS core level spectra acquired on PVdF binder-free NCA electrodes comparing pristine, fully de-lithiated at 4.9 V and fully lithiated at 3.0 V electrodes.

Unlike the carbon signal, the F 1s and P 2p core level signals increase at 4.9 V and remain visible at 3.0 V. The F 1s and P 2p peaks are located at 685.3 eV and 136.0 eV, respectively, associated with the LiF and PO_xF_y species originating from the LiPF_6 oxidation.⁴⁴ We also investigated with XPEEM the evolution of the LiF and Li carbonate species locally on the NCA and the carbon particles after long-term cycling (100 cycles) up to 4.9 V. Figure 7(a) presents the elemental contrast image after long-term cycling at the Ni L-edge and C and F K-edges. It can be observed that the NCA and conductive carbon are still visible, excluding the presence of a thick surface layer. In fact, the C and F K-edge spectra collected on NCA and conductive carbon particles [Figs. 7(b) and 7(c)] show the absence of carbonate species and the presence of traces of LiF species. This observation proves that during long-term cycling, the LiF does not grow continuously. However, we see that the LiF signal increases on the areas of the PVdF binder, which we associate with binder degradation at high potential, a conclusion that will be further supported in Sec. III D, where we discuss the results for the LTO counter electrode.

D. LTO surface evolution—Crosstalk between the cathode and the anode

The so-called “crosstalk” effect refers to the possible migration/diffusion of oxidized electrolyte and/or binder byproduct species and TMs from the cathode to the anode. Such species deposited on the anode can have a direct impact on the overall battery performance. To address the role of the “crosstalk” effect, we investigated the surface evolution of the LTO counter electrode when cycled vs NCA to 4.9 V during the early stages of cycling and after long-term cycling. Again, XPEEM and XPS measurements are combined to evaluate the possible poisoning of the LTO surface with (i) TMs, (ii) fluorine species, and (iii) carbonate species originating from the surface structural degradation of the NCA particles, decomposition of the PVdF and LiPF_6 , and oxidation of the solvents (EC, DMC), respectively.

FIG. 7. (a) XPEEM elemental contrast image for a long-term cycled NCA electrode and acquired at the Ni L-edge and C and F K-edges. (b) C K-edge and (c) F K-edge XAS measurements performed locally on NCA and conductive particles.

1. Electrolyte and PVdF binder decomposition at high voltage

The PVdF binder stability at 4.9 V and its possible migration/diffusion to the counter electrode are monitored via the F 1s core level XPS spectra. The spectra in Fig. 8(a) were acquired on the LTO binder-free electrode using LC30 electrolyte to avoid F contribution to the spectra from either the PVdF binder at the anode or the LiPF_6 salt. As expected, the fluorine signal is absent on the pristine electrode, while a fluorine peak is observed at 4.9 V and

remains at 3.0 V, located at 685.2 eV. The fluorine peak is attributed to the formation of LiF caused by the decomposition of PVdF⁴⁷ on the NCA electrode at high voltage and the subsequent deposition on the LTO electrode. The formation of LiF is further enhanced after long-term cycling of the cell with an LTO electrode vs NCA to 4.9 V in LP30 electrolyte [Fig. 8(b)]. The strong increase in the LiF signal is also caused in the latter case by the LiPF_6 salt decomposition at the cathode-electrolyte interface,^{48,49} since the long cycling measurement was performed on a cathode material mixed with the PVdF binder and using LP30 electrolyte.

FIG. 8. F 1s XPS core level spectra acquired on (a) the LTO binder-free electrode cycled vs NCA in LC30 electrolyte, (b) LTO with PVdF binder electrodes cycled vs NCA in LP30 electrolyte, showing the increase in LiF due to both LiPF_6 and binder decomposition, and (c) C K-edge spectra from the LTO electrode cycled vs NCA, acquired locally on conductive carbon after the first charge at 4.3 V and 4.9 V and after long-term cycling to the same potentials, showing the absence of any carbonate species at 290.4 eV.

Again, thanks to the good lateral resolution of the XPEEM, the possible migration/diffusion of oxidized EC and DMC solvent byproducts can be ascertained. The investigation of the electrolyte byproducts is possible because the reduction of the carbonate-based electrolyte can occur on the LTO electrode along the plateau at 1.55 V vs Li^+/Li via a process that solely involves the particles of LTO active material, whereas the conductive carbon remains free from any detectable surface layer.²⁵ Thus, the detection of any surface evolution on conductive carbon particles, when LTO is cycled vs high-potential cathode materials, is a direct proof of “crosstalk” of organic–inorganic side reaction species formed at the cathode surface. Despite the high potential of 4.9 V, no carbonate species were detected on the carbon particles of the anode even after long-term cycling [Fig. 8(c)]. These findings suggest that, when NCA is cycled in LP30 electrolyte, even up to very positive potentials, the solvents appear to be inert since signs of oxidized solvent byproducts are detected neither on NCA nor on the LTO counter electrode. However, this is of course true only for reaction byproducts deposited on the surfaces. The reaction byproducts can dissolve in the electrolyte without forming an organic–inorganic layer on the anode or the cathode, e.g., by forming CO_2 or soluble molecules.

2. TM dissolution and deposition on the counter electrode

The possible poisoning of the LTO counter electrode by TMs leached from the NCA particles was investigated by performing XPEEM and XPS measurements on LTO electrodes after long-term cycling vs NCA with cutoff voltages of 4.3 V and 4.9 V. The Ti and Ni L-edge XPEEM elemental contrast images presented in Figs. 9(a) and 9(b) show that the surface of LTO is, indeed, covered by Ni and Co when the cutoff potential of the NCA is 4.9 V, while for the lower cutoff potential of 4.3 V, the LTO surface is free of detectable TMs. This observation is in line with previous studies⁴⁹ and with the above conclusion that the inactive layer with reduced TMs at 4.3 V is much thicker than the one at 4.9 V, where the dissolution of the reduced TMs into the electrolyte leads to thinning of the inactive layer. Figure 9(c), showing that both Ni and Co are in a mixed reduced metallic and oxidized +2 state, is an indication of a very complex chemical reactivity which these TM compounds can present when they are in an environment containing fluorine and carbonate species. The Ni 3p XPS core level spectra presented in Fig. 9(d) confirm the XPEEM results by showing the presence of Ni on LTO when it is cycled vs NCA to 4.9 V and no Ni signal after cycling to 4.3 V.

E. Impact of the surface side reactions on the electrochemical performance

The effect of the above mentioned surface parasitic reactions on the strong fading of the cells during cycling [Fig. 1(b)] is investigated by harvesting long-term cycled electrodes and cycling them separately vs metallic lithium. In Fig. 10, we show the specific charge of NCA cycled vs LTO to an upper cutoff potential of 4.9 V. After 88 cycles (the cell was stopped in the discharged state, i.e., NCA in the lithiated state and LTO in the de-lithiated state), both electrodes were harvested and then cycled individually in fresh electrolyte vs metallic Li. The specific charge vs cycle plot shows, as expected, the strong capacity fading in the full-cell configuration. However,

FIG. 9. XPEEM elemental contrast images from Ti (blue) and Ni (red) L-edges of LTO electrodes after long-term cycling vs NCA with cutoff voltages of (a) 4.3 V and (b) 4.9 V. (c) Local Ni and Co L-edge XAS of the LTO electrodes showing the presence of TMs in an intermixed metallic and +2 oxidation state. (d) Ni 3p and Co 3p XPS core level spectra acquired on long-term cycled LTO vs NCA.

after harvesting the electrodes, we observe a slight increase in the specific charge of NCA by 18 mAh/g, corresponding to “dead Li” unable to cycle in the full-cell configuration. This dead (bound) Li is believed to be associated with the LiF formation caused by the PVdF binder and LiPF_6 salt degradation. In fact, the recovered 18 mAh/g is in line with the 23 mAh/g of specific charge difference obtained between the half cell and the full cell after long-term cycling presented in Fig. 1(b). Afterward, the specific charge of NCA continuously fades following the same trend as documented in Fig. 1(a). Surprisingly, the LTO counter electrode behaves differently, namely, it is able to recover the original specific charge and remains stable for the following 90 cycles. These findings suggest that the “crosstalk” of organic and inorganic species and transition metals has a limited, if any, impact on the LTO electrochemical performance. The fading observed in the full-cell configuration is, therefore, linked to the NCA electrode as suggested previously in several reports,^{10,14,45} where the surface of NCA and the PVdF binder degradation can have a direct impact. We also cannot exclude the strong effect of micro-crack formation that is often observed on this family of materials leading to an electrical isolation of active particles.^{15,21}

FIG. 10. Electrochemical performance of the NCA vs LTO cells cycled in LP30 electrolyte to the upper cutoff potential of 4.9 V (black dots). Harvested NCA (red dots) and LTO (blue dots) electrodes cycled in the half-cell configuration vs metallic lithium.

IV. CONCLUSIONS

The surface evolution of NCA based commercial-like electrodes and the “crosstalk” effect of organic–inorganic species and TMs in cells with an LTO counter electrode have been investigated post mortem at multi-length scales, using x-ray spectroscopy. By combining the high lateral resolution and surface sensitivity of XPEEM with XPS and XAS with different depths of analysis using TEY and TFY detection modes, we were able to obtain a full picture of the various reactions taking place at the electrode–electrolyte interface. We demonstrated that the first surface modification of NCA occurs while storing the powder in ambient air, where the reaction with ambient moisture and CO₂ leads to the formation of a carbonate-rich layer responsible for the very high overpotential observed during the very first de-lithiation phase. Such a carbonate layer incorporates Ni and Co in a reduced +2 oxidation state; it is unstable and dissolves during the first cycle above 3.8 V vs Li⁺/Li, leaving behind a “fresh,” bulk-like, NCA surface with Ni and Co in +3 oxidation states. We show that charge compensation takes place above 4 V by oxidizing simultaneously both Ni and oxygen, while Co does not participate in the redox reactions and remains in the +3 oxidation state during the whole redox process. We also demonstrate the formation of an inactive surface layer already at 4.3 V, rich in reduced Ni and depleted in oxygen. Nevertheless, at 4.9 V, a NiO-like structure is detected, accompanied with the formation of reduced Co, together with strong leaching of transition metals followed by their migration/diffusion to the LTO counter electrode. Solvent (EC, DMC) and salt (LiPF₆) oxidation and PVdF binder degradation were also elucidated, attesting (i) the absence of oxidized solvent byproducts on both NCA and LTO surfaces and (ii) the formation of LiF species on both NCA and LTO, caused by the salt and binder instability at high voltages. Finally, we addressed the electrochemical performance of NCA vs LTO cells cycled at 4.9 V to show that: (i) the poisoning of the LTO electrode with LiF and TMs has a very limited impact on the LTO electrochemical performance, (ii) immobile Li ions are related mainly to the formation of LiF, and (iii) the major fading of the cell is assigned to the

structural and mechanical degradation of the NCA electrode caused by the surface modification, PVdF binder instability, and micro-crack formation, leading all together to the formation of a presumably resistive surface layer and/or the electrical isolation of active particles.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for additional SEM and XPEEM images, XAS and XPS spectra, and electrochemical data. Calculations of the charge contribution from the carbonate dissolution are also presented.

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DATA AVAILABILITY

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

REFERENCES

- N. Nitta, F. Wu, J. T. Lee, and G. Yushin, *Mater. Today* **18**(5), 252–264 (2015).
- F. Schipper, P. Nayak, E. Erickson, S. Amalraj, O. Srur-Lavi, T. Penki, M. Talianker, J. Grinblat, H. Sclar, O. Breuer, C. Julien, N. Munichandraiah, D. Kovacheva, M. Dixit, D. Major, B. Markovsky, and D. Aurbach, *Inorganics* **5**(2), 32 (2017).
- G. E. Blomgren, *J. Electrochem. Soc.* **164**(1), A5019–A5025 (2017).
- P. He, H. Yu, D. Li, and H. Zhou, *J. Mater. Chem.* **22**(9), 3680–3695 (2012).
- T. Ohzuku, A. Ueda, and M. Kouguchi, *J. Electrochem. Soc.* **142**(12), 4033–4039 (1995).
- E. Jo, S. Hwang, S. M. Kim, and W. Chang, *Chem. Mater.* **29**(7), 2708–2716 (2017).
- J. Shim, R. Kostecki, T. Richardson, X. Song, and K. A. Striebel, *J. Power Sources* **112**(1), 222–230 (2002).
- D. P. Abraham, E. M. Reynolds, E. Sammann, A. N. Jansen, and D. W. Dees, *Electrochim. Acta* **51**(3), 502–510 (2005).
- A. M. Andersson, D. P. Abraham, R. Haasch, S. MacLaren, J. Liu, and K. Amine, *J. Electrochem. Soc.* **149**(10), A1358–A1369 (2002).
- S. Hwang, W. Chang, S. M. Kim, D. Su, D. H. Kim, J. Y. Lee, K. Y. Chung, and E. A. Stach, *Chem. Mater.* **26**(2), 1084–1092 (2014).
- S.-M. Bak, K.-W. Nam, W. Chang, X. Yu, E. Hu, S. Hwang, E. A. Stach, K.-B. Kim, K. Y. Chung, and X.-Q. Yang, *Chem. Mater.* **25**(3), 337–351 (2013).
- B.-s. Liu, Z.-B. Wang, F.-D. Yu, Y. Xue, G.-j. Wang, Y. Zhang, and Y.-X. Zhou, *RSC Adv.* **6**(110), 108558–108565 (2016).
- J. Hong, H.-D. Lim, M. Lee, S.-W. Kim, H. Kim, S.-T. Oh, G.-C. Chung, and K. Kang, *Chem. Mater.* **24**(14), 2692–2697 (2012).
- R. Robert and P. Novák, *J. Electrochem. Soc.* **162**(9), A1823–A1828 (2015).
- P.-C. Tsai, B. Wen, M. Wolfman, M.-J. Choe, M. S. Pan, L. Su, K. Thornton, J. Cabana, and Y.-M. Chiang, *Energy Environ. Sci.* **11**(4), 860–871 (2018).
- T. Hayashi, J. Okada, E. Toda, R. Kuzuo, N. Oshimura, N. Kuwata, and J. Kawamura, *J. Electrochem. Soc.* **161**(6), A1007–A1011 (2014).
- R. Robert, C. Bünzli, E. J. Berg, and P. Novák, *Chem. Mater.* **27**(2), 526–536 (2015).

- ¹⁸M. 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.* **6**(22), 4653–4672 (2015).
- ¹⁹F. Lin, I. M. Markus, D. Nordlund, T.-C. Weng, M. D. Asta, H. L. Xin, and M. M. Doeff, *Nat. Commun.* **5**, 3529 (2014).
- ²⁰E. Flores, N. Vonrüti, P. Novák, U. Aschauer, and E. J. Berg, *Chem. Mater.* **30**(14), 4694–4703 (2018).
- ²¹A. Grenier, H. Liu, K. M. Wiaderek, Z. W. Lebens-Higgins, O. J. Borkiewicz, L. F. J. Piper, P. J. Chupas, and K. W. Chapman, *Chem. Mater.* **29**(17), 7345–7352 (2017).
- ²²M. Mirolo, D. Leanza, L. Höltschi, C. Jordy, V. Pelé, P. Novák, M. El Kazzi, and C. A. F. Vaz, *Anal. Chem.* **92**(4), 3023–3031 (2020).
- ²³N. Gauthier, C. Courrèges, L. Goubault, J. Demeaux, C. Tessier, and H. Martinez, *J. Electrochem. Soc.* **165**(13), A2925–A2934 (2018).
- ²⁴D. Leanza, M. Mirolo, C. A. F. Vaz, P. Novák, and M. ElKazzi, *Batteries Supercaps* **2**(5), 482–492 (2019).
- ²⁵D. Leanza, C. A. F. Vaz, I. Czekaj, P. Novák, and M. El Kazzi, *J. Mater. Chem. A* **6**(8), 3534–3542 (2018).
- ²⁶C. A. F. Vaz, A. Kleibert, and M. El Kazzi, “Nanoscale XPEEM spectro-microscopy,” in *21st Century Nanoscience A Handbook* (CRC Press, 2020), Vol. 3, Chap. 17.
- ²⁷R. Jung, R. Morasch, P. Karayaylali, K. Phillips, F. Maglia, C. Stinner, Y. Shao-Horn, and H. A. Gasteiger, *J. Electrochem. Soc.* **165**(2), A132–A141 (2018).
- ²⁸G. V. Zhuang, G. Chen, J. Shim, X. Song, P. N. Ross, and T. J. Richardson, *J. Power Sources* **134**(2), 293–297 (2004).
- ²⁹K. Matsumoto, R. Kuzuo, K. Takeya, and A. Yamanaka, *J. Power Sources* **81–82**, 558–561 (1999).
- ³⁰J. Sicklinger, M. Metzger, H. Beyer, D. Pritzl, and H. A. Gasteiger, *J. Electrochem. Soc.* **166**(12), A2322–A2335 (2019).
- ³¹L. A. Montoro, M. Abbate, and J. M. Rosolen, *J. Electrochem. Soc.* **147**(5), 1651–1657 (2000).
- ³²W.-S. Yoon, K. Y. Chung, J. McBreen, D. A. Fischer, and X.-Q. Yang, *J. Power Sources* **174**(2), 1015–1020 (2007).
- ³³S. Sallis, N. Pereira, P. Mukherjee, N. F. Quackenbush, N. Faenza, C. Schlueter, T.-L. Lee, W. L. Yang, F. Cosandey, G. G. Amatucci, and L. F. J. Piper, *Appl. Phys. Lett.* **108**(26), 263902 (2016).
- ³⁴R. Qiao, Y.-D. Chuang, S. Yan, and W. Yang, *PLoS One* **7**(11), e49182 (2012).
- ³⁵S. Zheng, R. Huang, Y. Makimura, Y. Ukyo, C. A. J. Fisher, T. Hirayama, and Y. Ikuhara, *J. Electrochem. Soc.* **158**(4), A357–A362 (2011).
- ³⁶W.-S. Yoon, K.-B. Kim, M.-G. Kim, M.-K. Lee, H.-J. Shin, J.-M. Lee, J.-S. Lee, and C.-H. Yo, *J. Phys. Chem. B* **106**(10), 2526–2532 (2002).
- ³⁷D. Leanza, C. A. F. Vaz, G. Melinte, X. Mu, P. Novák, and M. El Kazzi, *ACS Appl. Mater. Interfaces* **11**(6), 6054–6065 (2019).
- ³⁸H. Zhang, B. M. May, F. Omenya, M. S. Whittingham, J. Cabana, and G. Zhou, *Chem. Mater.* **31**(18), 7790–7798 (2019).
- ³⁹K. 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.* **8**, 684 (2016).
- ⁴⁰K. Luo, M. R. Roberts, N. Guerrini, N. Tapia-Ruiz, R. Hao, F. Massel, D. M. Pickup, S. Ramos, Y.-S. Liu, J. Guo, A. V. Chadwick, L. C. Duda, and P. G. Bruce, *J. Am. Chem. Soc.* **138**(35), 11211–11218 (2016).
- ⁴¹W. E. Gent, K. Lim, Y. Liang, Q. Li, T. Barnes, S.-J. Ahn, K. H. Stone, M. McIntire, J. Hong, J. H. Song, Y. Li, A. Mehta, S. Ermon, T. Tylliszczak, D. Kilcoyne, D. Vine, J.-H. Park, S.-K. Doo, M. F. Toney, W. Yang, D. Prendergast, and W. C. Chueh, *Nat. Commun.* **8**(1), 2091 (2017).
- ⁴²J. Wu, Z. Zhuo, X. Rong, K. Dai, Z. Lebens-Higgins, S. Sallis, F. Pan, L. F. J. Piper, G. Liu, Y.-d. Chuang, Z. Hussain, Q. Li, R. Zeng, Z.-x. Shen, and W. Yang, *Sci. Adv.* **6**(6), eaaw3871 (2020).
- ⁴³Z. W. Lebens-Higgins, N. V. Faenza, M. D. Radin, H. Liu, S. Sallis, J. Rana, J. Vinckeviciute, P. J. Reeves, M. J. Zuba, F. Badway, N. Pereira, K. W. Chapman, T.-L. Lee, T. Wu, C. P. Grey, B. C. Melot, A. Van Der Ven, G. G. Amatucci, W. Yang, and L. F. J. Piper, *J. Mater. Horiz.* **6**(10), 2112–2123 (2019).
- ⁴⁴A. Guéguen, D. Streich, M. He, M. Mendez, F. F. Chesneau, P. Novák, and E. J. Berg, *J. Electrochem. Soc.* **163**(6), A1095–A1100 (2016).
- ⁴⁵K. Kleiner, J. Melke, M. Merz, P. Jakes, P. Nagel, S. Schuppler, V. Liebau, and H. Ehrenberg, *ACS Appl. Mater. Interfaces* **7**(35), 19589–19600 (2015).
- ⁴⁶M. Moshkovich, M. Cojocar, H. E. Gottlieb, and D. Aurbach, *J. Electroanal. Chem.* **497**(1), 84–96 (2001).
- ⁴⁷L. Bodenes, R. Dedryvère, H. Martinez, F. Fischer, C. Tessier, and J.-P. Pèrès, *J. Electrochem. Soc.* **159**(10), A1739–A1746 (2012).
- ⁴⁸Z. W. Lebens-Higgins, S. Sallis, N. V. Faenza, F. Badway, N. Pereira, D. M. Halat, M. Wahila, C. Schlueter, T.-L. Lee, W. Yang, C. P. Grey, G. G. Amatucci, and L. F. J. Piper, *Chem. Mater.* **30**(3), 958–969 (2018).
- ⁴⁹N. V. Faenza, Z. W. Lebens-Higgins, P. Mukherjee, S. Sallis, N. Pereira, F. Badway, A. Halajko, G. Ceder, F. Cosandey, L. F. J. Piper, and G. G. Amatucci, *Langmuir* **33**(37), 9333–9353 (2017).