Supporting Information

Transition metal dissolution and deposition in Li-ion batteries
investigated by operando x-ray absorption spectroscopy

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1) Electrode preparation and cell assembly

Cathodes based on commercial LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ (NMC) active material were prepared by dispersing NMC (96 wt%), polyvinylidene difluoride (PVdF, KynarHSV 900, Arkema, France) (2 wt%), and carbon black (Super C65, TIMCAL, Switzerland) (2 wt%) in N-methyl-2-pyrrolidone (NMP, Sigma Aldrich, Germany) and mixing them altogether in a planetary centrifugal vacuum mixer (Thinky, USA) at 2000 rpm for 15 min. The resulting viscous slurry with a solid content of 1.9 g/mL was cast onto a thin aluminum foil (thickness 18 µm, MTI corporation, USA) using the doctor blade method (RK Print Coat Instruments, UK) with a wet-film thickness of 240 µm. Graphite electrodes were produced analogously, using a mixture of 90 wt% graphite (Timcal, Germany) and 10 wt% PVdF binder in NMP (solids content of 0.88 g/ml) and a copper foil as current collector (10µm, MTI corporation, USA). After drying at room temperature, electrodes with a size of 10×10 mm (squares) were punched out and dried under dynamic vacuum for 12 hours at 120 °C (Büchi, Switzerland) and transferred into an Argon filled glove box (MBRAUN). Active material loadings were about 14.8 mg cm$^{-2}$ for graphite and 18.0 mg cm$^{-2}$ for NMC electrodes. NMC electrodes were compressed at a pressure of 130 MPa to a thickness of 125 µm and a porosity of 30%; graphite electrodes were used without compression (170 µm thickness, 50% porosity).

![Figure S1 Schematic drawing of the spectro-electrochemical operando XAS cell showing the incorporation of the reference electrode. A detail exploded view and description of the cell design is provided in reference [1].](image)

The XAS cell design is described in detail elsewhere.$^{[1]}$ It has been slightly modified in comparison to the work by Gorlin et al.$^{[1]}$ in order to accommodate a metallic lithium reference electrode as shown in Figure S1. The lithium reference electrode was placed in a central position underneath the electrode stack and contacted through a screw in the back
plate of the cell. The x-ray window consisted of an aluminized 12 µm Kapton® foil (aluminized side placed towards the cell exterior) and an additional 25 µm Kapton® foil (placed on top of the aluminum layer) to prevent mechanical damage of the thin aluminum layer. The cell was assembled with two glassfiber separators (250 µm uncompressed thickness, glass microfiber filter 691, VWR) and 300 µL electrolyte (1 MLiPF₆ in EC/EMC 3:7, BASF).

2) Electrochemical testing

Electrochemical testing was carried out using a Biologic SP200 battery cycler. Two different cycling procedures were used within this project. For the *operando* procedure (s. Fig. 1), the cell was mounted in the XAS sample stage directly after assembly and then cycled for two cycles between 3.0 and 4.6 V with a C/2 CCCV charge (C/20 current cut off) and 1C CC discharge followed by a single CC charge to 4.6 V followed by another CV step. The discharge capacities in the first two cycles were 174 mAh g⁻¹ NMC-1 and 169 mAh g⁻¹ NMC-1, respectively. The potential was then increased with a sweep rate of 2.5 mV min⁻¹ to 5.0 V, where it was held for 200 minutes. A second cell (“conventional cycling procedure”) was cycled inside the glovebox for 22 cycles between 3.0 and 4.6 V: after a C/10 formation cycle, the cell was cycled with a C/2 CCCV charge (C/20 current cut off) and 1C CC discharge. The last cycle showed a discharge capacity retention of 169 mAh g⁻¹ NMC-1, which is comparable to the performance in a standard Swagelok cell. [2] After cycling, the cell was sealed in a pouch bag inside the glove box and transported to the synchrotron in the charged state, thus eliminating the possibility of oxygen intrusion. After mounting the cell in the sample stage, XAS spectra were recorded in the charged state (graphite potential +0.095 V vs. Li/Li⁺) and in the entirely discharged state (graphite potential +1.5 V vs. Li/Li⁺).

3) XAS experiments

The X-ray absorption spectra were measured at the SAMBA beamline, a hard X-ray bending magnet beamline at Soleil synchrotron, France. The acquisition time for each spectrum presented in this work was approximately 24 minutes. The synchrotron was operating in multibunch top up mode. A sagittaly focusing double crystal monochromator consisting of two Si 220 crystals was used to select the incoming energy and the beam was focused using Pd coated mirrors before being cut with slits to achieve a beam size of 100 micrometer in the horizontal and approximately 1000 micrometer in the vertical dimension. The cells were
assembled as described above, and measured in fluorescence mode, with an energy selective Canberra 35-element monolithic planar Ge pixel array detector to collect the photons. Photon energies were calibrated using the first peak in the first derivative of the pure metal foils, which were measured in fluorescence before and after the operando studies, and background corrections of the spectra were carried out using the IFEFFIT software package.\textsuperscript{[3,4]}

4) Manganese K-edge spectrum of electrolyte

Figure S2 shows a manganese K-edge spectrum measured in the electrolyte (separator position, pink line) during the 5 V constant potential step as indicated in Figure 1c (main paper). The oxidation state of the dissolved manganese is clearly +2 which is consistent with the literature.\textsuperscript{[5]}

The XAS spectra, which are measured in the graphite position actually show a superposition of manganese deposited on the surface of the graphite particles and manganese species dissolved in the electrolyte which is contained within the pores of the graphite electrode (50% porosity). It is therefore only possible to reliably determine the oxidation state of manganese deposits on the graphite electrode, if the spectrum measured in the graphite position is dominated by manganese deposits rather than by dissolved manganese species. The edge jump measured in the separator (Figure S2) corresponds to a manganese concentration of about 2.2 mmolar (s. filled pink star at \(\approx\)13 h in the lower panel of Fig. 1c). If the concentration of the dissolved manganese species was constant across the entire cell, the dissolved manganese species would correspond to a \(\approx\)1.1 mmolar concentration in the graphite position considering the porosity of the graphite electrode of 50% (s. empty pink star at \(\approx\)13 h in the lower panel of Fig. 1c). If one interpolates the manganese concentration determined in the graphite position directly before and after the separator spectrum to the time at which the separator spectrum was measured, one contains a manganese concentration of 3.2 mmolar for the graphite position. Therefore, at this point in time (about 13 hours) the higher limit for the contribution of dissolved manganese to the spectrum measured in the graphite position can be estimated to be about 25% \((=1.1/(1.1+3.2))\). The real contribution of the dissolved manganese will be significantly smaller due to two reasons: Firstly, the above estimation is based on the assumption that the concentration of dissolved manganese is identical (1.1 mmolar) for electrolyte contained within the pores of
the graphite electrode and the separator. In reality, the manganese is being released into the electrolyte at the NMC electrode and then diffuses through the separator to the graphite electrode. As this diffusion is driven by a concentration gradient, the manganese concentration has to be lower in the electrolyte contained in the graphite electrode in comparison to the electrolyte contained in the separator, which is closer to the NCM electrode. Secondly, the fact that manganese is being accumulated in the graphite electrode means that it is being extracted from the electrolyte. As a direct consequence, the manganese concentration in the electrolyte contained within the porous graphite electrode is further reduced in comparison to the respective concentration in the separator. Therefore, the manganese K-edge spectra measured within the graphite electrode during the 5V hold step can reliably be assigned to manganese deposits.

![Mn K-edge spectra](image)

**Figure S2** Mn K-edge spectra of reference compounds as well as *operando* spectrum measured in the electrolyte (= separator position) at the beginning of the 5 V potential hold after the initial charge/discharge cycles in the operando XAS cell. The exact time at which the *operando* spectrum was measured is indicated by the pink star at the right-hand-side of the lower panel of Figure 1c (main text).

The situation is a little less clear in the initial spectra due to the lower difference in the manganese concentration measured in the graphite position (0.9 mmolar) in comparison to the electrolyte (1.3 mmolar, or 0.65 mmolar considering 50 % porosity of the graphite
electrode; see full and empty pink star near 0 h in the lower panel of Fig. 1c). Accordingly, the contribution of dissolved manganese to the first manganese spectrum measured in the graphite position can be estimated to be about 42% (=0.65/(0.65+0.9)). Nevertheless, the main conclusion derived from the manganese spectra in the graphite position, that the manganese deposits are always present in oxidation state +2 irrespective of the graphite potential, is in no way hampered by the slight contribution of dissolved manganese in the initial spectra.

5) Analysis of manganese oxidation states

The edge positions of the Mn samples were determined by taking the position of the second peak in the 1st derivative of the K-edge XANES spectra. In Figure S3 the edge positions of all Mn references (black points) are plotted against formal oxidation state in order to more clearly see the trend in edge shifts. From this it is clear that the edge position of the final operando graphite spectrum (red point) is consistent with the values obtained for a formal oxidation state of +2. A linear fit is not possible due to the rather wide range of edge values for a single oxidation state, as demonstrated by the values obtained for Mn$^{2+}$, due to the fact that the edge values for transition metals also depend on geometry and ligand coordination.[6] The relatively poor signal-to-noise ratio for the 1st derivative spectrum of the ex situ sample makes assigning a precise edge position difficult, this is further discussed below. The references measured were as follows: Mn foil (Mn(0)), MnO (Mn(II)), Mn(CH$_3$COO)$_2$·4H$_2$O (Mn(III)), manganocene (Mn(II)), Mn$_2$O$_3$ (Mn(III)), MnO$_2$ (Mn(IV)), and pristine NMC material (Mn(IV)). All Mn references were purchased from Sigma-Aldrich (Germany), with the exception of the NMC material (see above). Pellets were prepared using boron nitride as a diluent and measured in transmission. The 1st derivative XANES spectrum of the ex situ graphite sample (Figure S4, blue line) shows a broad peak at the edge position (6542-6550 eV) which has intensity spanning the edge position for Mn(0) and Mn(II), as depicted here by spectra from a Mn foil (black line) and Mn(II)(CH$_3$COO)$_2$·4H$_2$O (red line). Therefore, we believe a combination of Mn(0) and Mn(II) is present, both in significant amounts. This is supported by an examination of the associated XANES spectra (Figure S4), which shows that the rising edge is located between those of Mn foil and Mn(II)(CH$_3$COO)$_2$·4H$_2$O. Unfortunately, due to the data quality and lack of suitable reference spectra further analysis by principle components analysis is not possible.
Figure S3: Edge position in Mn K-edge spectra for several reference compounds (black dots) as a function of their formal oxidation state and the final *operando* spectrum measured on the graphite electrode (red dot, see Figure 2b in main text). The final *operando* spectrum occurs at the same energy as manganocene, so the two data points are overlaid.

Figure S4: Mn K-edge XANES spectra (left) and the 1st derivative Mn K-edge XANES spectra (right) of the ex situ graphite sample overlaid with the spectra of Mn (II) acetate and Mn foil reference samples to demonstrate relative edge positions.
6) Quantification of transition metal deposition on graphite

In order to quantify the amount of transition metal deposited on the graphite electrode, calibration curves (Figure S5) were measured containing manganocene, cobaltocene and nickelocene (all Sigma-Aldrich) in concentrations of zero (= background signal for pure electrolyte), 0.4, 4 and 20 mM dissolved in LP57 electrolyte. The calibration curves were measured directly in the *operando* XAS cell in the same geometry, thus eliminating the necessity of performing a correction for differences in x-ray penetration depths. For the calibration measurements, the cells contained only two glass fiber separators and no electrodes. The calibration can be used to convert experimentally determined edge jumps into concentrations (in mol L\(^{-1}\)). The experimentally determined transition metal concentrations are all in the low mmolar range, which is close to the detection limit for the XAS experiment; furthermore, the manganese and cobalt calibration curves show no ideal linear behavior in this concentration range (Figure S5). Accordingly, the transition metal concentrations determined by XAS will contain an error which cannot be exactly determined due to the non-linear behavior of the calibration curve in the relevant concentration range. Nevertheless, they present a reasonable estimate for the transition metal concentration.

![Calibration curves of manganocene, cobaltocene and nickelocene dissolved in LP57 electrolyte in concentrations of zero (= pure electrolyte), 0.4, 4 and 20 mM measured directly in the operando XAS cell.](image)

Figure S5 Calibration curves of manganocene, cobaltocene and nickelocene dissolved in LP57 electrolyte in concentrations of zero (= pure electrolyte), 0.4, 4 and 20 mM measured directly in the operando XAS cell.

By comparing the initial and the final XAS spectra measured in the operando cell, concentration increases during cycling of ≈ 3, 9, and 6 mmol L\(^{-1}\) were found for Mn, Co, and Ni, respectively (the Mn concentration increase is shown in the lower panel of Figure 1, main text). From this concentration increase, the total amount of each metal deposited on the
graphite electrode (in mol) can be calculated considering the volume of the graphite electrode, which equals $10 \text{ mm} \times 10 \text{ mm} \times 0.17 \text{ mm} = 17 \cdot 10^{-6} \text{ L}$. The relative amount of the dissolved transition metals can be calculated by dividing by the total amount of each transition metal in the NMC electrode (containing $17.08 \text{ mg LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ for this cell with a molecular weight of $96.46 \text{ g/mol}$), which is $59 \cdot 10^{-6} \text{ mol}$ for Mn, Co and Ni. Accordingly, the concentration increases over the entire course of the experiment ($3, 9$ and $6 \text{ mmol L}^{-1}$ for Mn, Co and Ni) can be converted into dissolution fractions of $0.09, 0.26$ and $0.17\%$ of the total metal content in the NMC electrode. These values agree within a factor of two with *ex-situ* ICP-OES analysis ($0.165 \pm 0.015 \%$ for Mn, $0.125 \pm 0.002 \%$ for Co and $0.116 \pm 0.002 \%$ for Ni) of harvested electrodes as explained in the next section.

For manganese, it is also possible to extract dissolution rates from the time resolved operando experiments shown in Figure 1 (main text). For the first two cycles between 3.0 and 4.6 V, an average dissolution rate of $0.34 \cdot 10^{-9} \text{ mol h}^{-1}$ can be estimated (based on the slope of $20 \mu\text{mol h}^{-1} \text{ L}^{-1}$ shown in the lower panel of Fig. 1c multiplied by the graphite electrode volume of $17 \cdot 10^{-6} \text{ L}$) which for an approximate cycle time of 3.5 h (s. upper panel of Fig. 1c) corresponds to a manganese loss of $\approx 1.0 \cdot 10^{-9} \text{ mol/cycle}$ or $=0.0017\%_{\text{Mn}}/\text{cycle}$. This may be compared to a previous study, where the same NMC material was cycled in a NMC/graphite full-cell in the same potential range (3.0/4.6 V) at similar conditions (1C CCCV charge (C/20 cut-off) and 1C discharge vs. 0.5C CCCV charge (C/20 cut-off) and 1C CC discharge in the present study), resulting in a total amount of Mn deposited on the graphite electrode of $0.35\%_{\text{Mn}}$ of the total Mn content of the NMC electrode (measured by post-mortem prompt-gamma-activation analysis). If normalized by the number of cycles, the latter value equates to $\approx 0.0015\%_{\text{Mn}}/\text{cycle}$, which is in excellent agreement with our XAS based measurements. At potentials above 4.6 V, the manganese dissolution rate equals $17 \cdot 10^{-9} \text{ mol h}^{-1}$ (based on the now higher slope of $1000 \mu\text{mol h}^{-1} \text{ L}^{-1}$ shown in the lower panel of Fig. 1c multiplied by the graphite electrode volume of $17 \cdot 10^{-6} \text{ L}$), which is $\approx 50$-fold higher than the rate found between 3.0 and 4.6 V.

In order to verify the amount of transition metal deposition on the graphite counter electrode with a second analytical technique, two nominally identical cells were cycled with the same procedure as shown in Figure 1c (upper panel). Directly after the end of the procedure, the graphite electrodes were harvested in the charged state, at the end of the
200 minute hold at 5 V. The copper current collector and glass fiber residue were removed and the graphite coating was immersed in 1 mL 65 %HNO$_3$ (analytical grade, Sigma Aldrich) for one week. The determination of the manganese, cobalt and nickel concentration in HNO$_3$ was then carried out by ICP-OES (Mikroanalytisches Labor Pascher, Remagen, Germany). The thus quantified metal content of the graphite electrode –expressed as fraction of the total metal content in the NMC electrode – amounts to 0.165 ± 0.015 % for Mn, 0.125 ± 0.002 % for Co and 0.116 ± 0.002 % for Ni, respectively (the error corresponds to the standard deviation from analyzing the graphite electrode harvested from the two nominally identical cells). For all three metals, the contents determined via operando XAS and ICP-OES are consistent within a factor of two (s. above). Note, however, that the trend is inverted, with cobalt showing the highest concentration in the XAS determination and manganese showing the highest concentration in the ICP-OES determination. It is not entirely clear whether the XAS or ICP-OES analysis is more accurate as both techniques contain possible sources of error which are difficult to quantify. One can therefore only conclude that the dissolution rate is in the same order of magnitude for all three transition metals without knowing exactly which metal shows the highest dissolution rate. In comparison, Gallus et al.[7] found very similar manganese, cobalt and nickel contents in the electrolyte after storage experiments whereas the post-mortem PGAA analysis by Buchberger et al.[2] found the manganese content to be twice as high as that of cobalt and nickel.

7) Estimation of redox potentials in carbonate based electrolytes

It is not possible to state exact potentials for the expected Mn(II), Co(II) and Ni(II) reduction potential vs. Li/Li$^+$ because, to the best of our knowledge, there is no consistent data for the redox potentials of these transition metals in carbonate based electrolytes. According to the standard electrode potential series in aqueous electrolyte, the Mn(0)/Mn(II) potential is about 900 mV more negative than the respective values for cobalt and nickel. If the redox potentials are corrected for the different solvation energies in water and ethylene carbonate,[8] the resulting redox potential of Mn(0)/Mn(II) is 690 mV more negative than Ni(0)/Ni(II) and 1100 mV more negative than Co(0)/Co(II). Accordingly, in carbonate based solutions the same trend in redox potentials holds true as in aqueous solutions with manganese being the least noble metal.
8) Mn-K edge spectra on graphite electrode after “conventional” cycling

For a description of the cycling procedure see Section 2 in the supplementary information.

Figure S6 Mn K-edge spectra of reference compounds and operando spectra of the graphite electrode either in the lithiated (at 0.095 V vs. Li/Li⁺) or delithiated (at 1.5 V vs. Li/Li⁺) state. The operando spectra were obtained with a Graphite/NMC operando XAS cell after 22 “conventional cycles” between 3.0 V and 4.6 V with 1M LiPF₆ in EC/EMC as electrolyte.
9) Optical images of lithiated graphite electrodes

![Graphite electrode images](image)

Figure S7 Graphite electrode harvested inside the glove box from Swagelok T-cells after finishing the same procedure which was conducted for the operando XAS measurements (s. upper panel of Fig. 1c in the main manuscript. The Images show the top side of the graphite electrode which had faced the NMC electrode during cycling: a) directly after harvesting the graphite electrode from the cell inside the glove box, b) after drying for 40 minutes in the glove box, c) after drying for 80 minutes in the glove box, d) after drying for 2 days in the glove box, and, e) after scratching off the top layer of the graphite electrode with a scalpel after two days of drying in the glove box.

References


