Crystal structure evolution via operando neutron diffraction during long-term cycling of customized 5 V full Li-ion cylindrical cells LiNi_{0.5}Mn_{1.5}O₄ vs. graphite

Lucien Boulet-Roblin¹⁺, Denis Sheptyakov^{2+*}, Philippe Borel³, Cécile Tessier³, Petr Novák¹, Claire Villevieille^{1*}

¹ Paul Scherrer Institute, Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland

² Paul Scherrer Institute, Laboratory for Neutron Scattering and Imaging, CH-5232 Villigen PSI, Switzerland

³ SAFT, 111 Boulevard Alfred Daney, F-33074 Bordeaux, France

⁺ These authors contributed equally to this work

Corresponding author: Claire.Villevieille@psi.ch, Denis.Cheptiakov@psi.ch

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Abstract

Disordered spinel LiNi_{0.5}Mn_{1.5}O₄ (d-LNMO) is the cathode material of choice for the next generation batteries based on 5 V systems. Unfortunately, once cycled under real conditions i.e. in full-cell configuration (versus graphite), it displays a quite pronounced fading of the electrochemical performance, even with optimized cycling conditions, and about a half of the specific charge is 'lost' after 500 cycles. Thus, we intensively investigated the crystal structure evolution of a full-cell d-LNMO vs. graphite by means of operando neutron diffraction. For this purpose, a new cylindrical electrochemical cell was designed, suitable for the operando neutron diffraction studies and allowing for precise Rietveld refinement analyses. During the first cycle, lithium content in the electrode materials (graphite and d-LNMO) could be determined, thus, allowing an estimation of the lithium consumption in side-reactions. The neutron diffraction data obtained after long-term cycling (100 cycles) show that the fading of the electrochemical performance can be attributed to an insufficient amount of lithium in the system, which presumably is being consumed by side-reactions since no structural damage was observed in the positive and negative electrodes.

Introduction

In recent years, renewable energies have gained momentum as more and more gigawatt production capabilities are being installed. However, the problem of especially renewable wind and solar energies is their intermittent nature. This drawback means that advanced energy storage is needed in conjunction with the renewable energy technology to even out the erratic energy production profile and to allow for shifts in the demand relative to the supply. One promising solution is offered by rechargeable batteries due to their scalable storage capacity, little restraints on location and their high storage efficiency. Today, batteries mainly serve the consumer electronics segment comprised of mobile phones, laptops and diverse power tools but the main growth in the Li-ion battery market is expected in mobility. To this point, novel battery types based on 5 V cathodes are expected to take the leadership since their industrial usage could result in at least 20% increase in energy density compared to common 4 V based batteries (i.e. LiFePO_4 -vs. graphite).

Along cycling, the reaction mechanism of a Li-ion battery is based on (de)lithiation of electroactive materials accompanied with changes in crystal structure. It is crucial to fully understand the mechanisms of such reactions in order to prevent possible damage of electrode materials leading to the battery failure. Disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (d-LNMO) spinel is a promising cathode material with an average working potential of 4.7 V vs. $\text{Li}^+/\text{Li}^{1-3}$. Once cycled versus Li metal, this cathode material might be considered stable with a relatively long cycling life. Changing the counter electrode from lithium metal to graphite (as in a commercial battery) leads to drastic fading of the electrochemical performance of the cells^{4, 5}. This degradation is caused by three main factors: i) electrolyte decomposition at high voltage^{6, 7}, ii) transition metal dissolution (Ni and Mn atoms migrate to the graphite counter electrode)⁸, and iii) lithium consumption, for example due to the formation of Solid Electrolyte Interphase (SEI) and lithiated decomposition products^{9, 10}. However, there is a certain lack of understanding of those processes and their relations to the structural changes occurring during (de)lithiation especially along ageing^{5, 11, 12}.

Only a few techniques allow following the degradation of both electroactive LNMO and graphite materials simultaneously. Neutron diffraction is one of the rare techniques allowing the determination of both the lithium content and structural changes occurring during cycling¹³⁻¹⁵. Unfortunately, the interaction between neutrons and matter is generally weak, and this inspires the development of new cell designs with larger amounts of electroactive materials for obtaining a good signal/noise ratio, which is often detrimental to obtain reliable electrochemical performance. Many cell designs for operando neutron diffraction measurements have been reported in the literature¹⁶⁻²¹. However, to the best of our knowledge, none of these have so far succeeded in getting the diffraction data quality suitable for studying the ageing reaction mechanisms with reliable Rietveld refinements. To understand the long-term cycling degradation mechanisms, the cells need to sustain several

cycles at low and/or fast rate with good electrochemical performance and allow for lithium determination from Rietveld refinement^{22, 23}. Cylindrical cells are known to cycle large amounts of active materials with excellent performance but, regrettably, their neutron diffraction patterns feature poor signal-to-noise ratios because of the large amount of hydrogen in the electrolyte/separator and numerous further cell parts^{24, 25}. In this paper, we present a novel electrochemical cell dedicated to operando neutron diffraction experiments that adhered to the following criteria: i) large amounts of electroactive materials (LNMO and graphite), ii) good electrochemical performance for both relatively fast (~ 1 C) and low ($\sim C/25$) rates (the 1 C rate is equivalent to 1 charge or discharge per hour), iii) long-term cycling stability, and iv) suitable to deliver neutron diffraction patterns of sufficient quality to allow for reliable Rietveld refinement analysis. We used this cell to study the materials ageing mechanisms in novel 5 V Li-ion batteries combining $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel material and graphite as counter electrode.

Experimental

Development of a reliable electrochemical cell suitable for neutron diffraction study (Figure 1)

Optimization of different parameters should be considered when designing reliable electrochemical cells with a large quantity of electroactive materials (3-4 grams per electrode, i.e. loadings higher than 20 mg/cm^2 of electrode material), which would as well deliver neutron diffraction patterns with the minimal signal from non-electroactive cell parts in the beam. The cell components inside a battery, such as the casing (usually iron) and electrolyte (composed of organic solvents and a salt), inevitably produce extra signals, thus generating a high background of incoherent scattering and strong Bragg peaks in the neutron diffraction data. Other components, such as the separator (typically a layer-type polymer containing hydrogen), the electrode film (typically Cu or Al metal foil as a current collector, coated with electroactive material of interest), and the binder (generally a polymer containing hydrogen and fluorine) also cause background noise, usually not flat or uniform, sometimes as well containing coherent diffraction peaks. The amount of contributing phases and associated scattering arising from the cell components are so high that a proper structural analysis of the electroactive materials with Rietveld refinement is almost impossible. Thus, in order to ensure a proper structural analysis, a compromise must be found between performing reliable electrochemistry with high amounts of active materials and achieving a reasonable signal/noise ratio. From the electrochemical point of view, the main targets are homogeneous current distribution along the electrode sheets, and avoiding any possible lithium gradients in the cell, which would result in an inhomogeneous reaction^{20, 21, 26, 27}.

Only a cylindrical cell design can fulfil the pre-requisites for both criteria. In a cylindrical design, the electrodes are rolled intimately inside each other, thereby improving the contact

between them, and avoiding an inhomogeneous reaction and lithium gradients. However, cylindrical designs require a large surface area electrode, and hence large current collectors, which increases the unwanted signal in the neutron diffraction pattern. The casing itself is a problem, since it is mainly composed of iron. The mandrel (rod used for rolling and keeping the electrodes together) is yet another source of additional background signal. In order to overcome these problems, we used the following strategies: the iron casing was replaced by a casing made of aluminum and the mandrel was removed prior to the neutron measurement. Finally, improvements have been made to the electrode composition. Usually, laboratory electrodes are obtained as a film by mixing the electroactive material with binder and conductive additives in an 80/10/10 wt.% ratio. However, as stated before, the binder and conductive additives generate strong noise in the neutron diffraction pattern. Thus, improved compositions were developed by applying extensive engineering experience, to reduce the binder and conductive additive content each to 4 wt.%, while increasing the content of electroactive materials from 80 to 92 wt.%. Similarly, the separator required optimization. Normally, the separator is a 25 μm thick polypropylene foil that generates a very high background and additional maxima in the neutron diffraction pattern. A composite separator composed of alumina (10-15 μm , quasi transparent to neutron diffraction) and PET (ca. 10 μm) offers an alternative that decreases drastically the intensity contribution of the separator to the background of neutron diffraction pattern while keeping reliable electrochemistry; addition of a well-known crystal structure of Al_2O_3 to the Rietveld refinement does not present hereby any serious obstacle. The final factor that required optimization was the electrolyte. The electrolytes for Li-ion batteries are typically composed of a salt dissolved in organic solvent, the high hydrogen content of which reduces the quality of the pattern, causing a too poor signal-to-noise ratio to ensure proper structural data analysis and good refinement quality. Having now used the deuterated solvents in our newest design, we minimize also this source of background, thus further improving the data quality. A lithium reference electrode was introduced in the 18650 cell in order to follow each electrode voltage independently. The Figure 1 shows the illustration of the cell showing its specific setup.

Figure 1. Scheme and photo of the cylindrical cell modified for operando neutron diffraction

Cycling protocol

After assembly, the cylindrical cells were dried at 50 °C overnight and then stored in an argon-filled glovebox. The cells were filled with deuterated LP30 electrolyte for operando measurements (~2 mL, 1 M LiPF₆ (Sigma-Aldrich) in 1:1 wt.%/wt.% deuterated ethylene carbonate/deuterated dimethyl carbonate (Armar Chemicals)) and a non-deuterated standard LP30 electrolyte (BASF) when mentioned in the text. The cycling of the cylindrical or standard cells was carried out galvanostatically between 3.5 and 4.8 V with a VMP-300 potentiostat (Bio-Logic) at room temperature (25 °C). The C-rates were calculated assuming experimental specific charges of 135 mAh/g for d-LNMO and 340 mAh/g for graphite. Prior to operando measurement, the cylindrical cell was pre-cycled (only one cycle) in the laboratory at the C/10 rate to ensure the deposition of a good SEI layer on the graphite electrode.

For the ex situ measurements, the cylindrical cells were charged to the desired voltage (4.5 or 4.75 V) at C/25 rate and held for 5 h in the potentiostatic mode (at given constant voltage). Then, the electrodes were extracted and washed in DMC (dimethyl carbonate) to remove remaining salts. Finally, the electrodes were gently scratched off from the current collectors, and the powder was placed into airtight vanadium containers.

Neutron diffraction set-up

The neutron powder diffraction (NPD) patterns were collected with the high resolution powder thermal neutron diffractometer HRPT at the Swiss Spallation Neutron Source (SINQ) at Paul Scherrer Institute. The neutron beam with a wavelength of 1.494 Å was obtained by using a (533) reflection from the vertically focusing Ge-monochromator. The instrument was used in a high intensity mode; each individual scan took about 2 min in the operando experiments. The background and any coherent scattering from the sample environment pieces or air around the cell on the sample table were effectively eliminated by the use of the

oscillating radial collimator. The diffraction signal was registered by a position-sensitive detector in the 2θ angular range between 5 and 165° . The cell was mounted straight over the middle of the sample table, thus horizontally and vertically matching the best beam conditions. The adjustable beam reduction in front of the sample table allowed for efficiently removing the scattering from unwanted pieces in the construction of the cylindrical cell, thus maximizing the peak to background ratio for exactly the region where the active materials were situated. The rectangular aperture of the beam was 20 mm high and 18 mm wide. Rietveld refinements of the diffraction patterns were performed using the FULLPROF package.²⁸

Results

Figure 2 (left) shows the galvanostatic profiles of the three electrode couples at a rate of C/20. The lithium reference electrode allows following the potential of d-LNMO vs. Li, and graphite vs. Li electrodes separately. The galvanostatic profiles are similar to those reported in the literature, demonstrating the reliability of the cell. The same conclusion is drawn for the graphite, whose potential evolution is similar to the data from the literature^{9, 29}. Figure 2 (right) shows the normalized practical capacity evolution of the full-cell d-LNMO vs graphite, obtained with our cylindrical cell and compared to a coin-cell type at a rate of C/10. Slightly lower practical capacity is obtained with the cylindrical cell, which can be explained by the higher loading of the electrodes, the current density distribution along the cell, and slightly weaker mechanical force that holds the electrodes together in the cylindrical cell upon removal of the inner core, compared to a standard coin-cell. Nevertheless, these results confirm that our cylindrical cell design shows reliable electrochemistry with the highly loaded electrodes.

Figure 2: (left) Galvanostatic profiles of d-LNMO vs graphite, d-LNMO vs. Li ref. and graphite vs. Li ref. electrodes at a rate of C/20; (right) Normalized capacity of d-LNMO vs. graphite cells (standard PSI and the new cylindrical cell for neutron diffraction) cycled at C/10 rate, in 3.5 V-

4.9 V potential windows. Open and filled symbols stand for specific charge and discharge, correspondingly.

Neutron diffraction experiments with the optimized cell

Figure S1 shows a comparison of the neutron diffraction patterns of a typical commercial cylindrical cell and of the cell we developed. Clearly, our new cell design has a better signal-to-noise ratio and delivers significantly higher diffraction intensity than the commercial cell despite the difference in data collection duration. Moreover, replacing the iron casing with aluminum one removes the strong iron contribution to the pattern at 155° , and some weaker peaks throughout the pattern. This improved cell design allows patterns to be collected in a time frame of 2 min at HRPT. The Rietveld refinement of the neutron diffraction pattern obtained prior to cycling at open circuit voltage (OCV) is presented in Figure 3, and Table S1 summarizes the refined crystal structure parameters of the graphite and d-LNMO phases. Five phases are needed to fully model the intensity in this pattern, including the two electroactive phases: d-LNMO and graphite materials, the cell parts (copper and aluminum of the current collectors and the cell casing), and the Al_2O_3 being part of the polymeric separator.

Figure 3: Rietveld refinement based on the neutron diffraction pattern of the new cylindrical cell recorded prior to cycling (30 min of acquisition). Experimental points, calculated profile, and difference curve are shown, the ticks below the graph correspond to the calculated positions of the diffraction peaks of the contributing phases.

The refined crystal structure parameters of both the d-LNMO and graphite phases are similar to those known from the literature^{30,31}. As expected, the diffraction lines of graphite are displaying pronounced anisotropic peak broadening.

Operando neutron diffraction during the first cycle

In the following section, the evolution of the most intense reflections in the diffraction pattern in course of charge-discharge cycling is followed. These are: the (222) reflection of d-LNMO, appearing at different stages of (de)lithiation between $\sim 37^\circ$ and $\sim 38^\circ$ in 2Θ , and the (002) peak of graphite, changing during the cycle into the corresponding reflections of the lithiated graphite derivatives, between $\sim 23^\circ$ and $\sim 26^\circ$. Observing the changes happening to these most representative reflections in the battery charge-discharge cycle, we will correlate those to the structural changes in the electroactive materials occurring during cycling.

Evolution of the cathode material d-LNMO

From the galvanostatic curves (Figure 4, right), we can distinguish three potential plateaus attributed to the transition $\text{Ni}^{2+} \rightarrow \text{Ni}^{4+}$. These are accompanied by a shift of the (222) Bragg reflection to a higher angle (Figure 4, left), indicating that a “solid-solution” reaction is taking place in which the lithium content in the structure decreases, accompanied by the corresponding decrease in the lattice parameters of the pristine d-LNMO phase (hereafter named ‘phase 1’). This shift is associated to a change in the oxidation state of nickel, with a decrease of the Ni-O bond length^{32, 33}. After ~ 15 h of charging, the diffraction pattern seems to get stabilized to that of a cubic structure with the same $Fd-3m$ space group, but shorter lattice constant. This stable phase (hereafter referred to as ‘phase 2’) is stabilizing at the end of the second potential plateau³⁴. At this stage, it is important to note that phases 1 and 2 do not coexist. Pursuing the delithiation of phase 2 leads to a two-phase reaction that occurs during the last potential plateau (from ~ 4.7 V to 4.8 V) and corresponds to the transition $\text{Ni}^{3+} \rightarrow \text{Ni}^{4+}$. This transition leads to the appearance of a new phase, with a characteristic diffraction peak at $\sim 37.80^\circ$, which is referred to as ‘phase 3’. Phase 3 also has a cubic structure with the same $Fd-3m$ space group, and lithium content in it is close to zero^{34, 35}. At the end of the charge process, we still find a small portion of the half-delithiated phase 2, which confirms that the reaction was not complete, even at a slow rate with a potentiostatic step. Our Rietveld refinements indicate that $\sim 97(1)\%$ of the lithium was extracted from the d-LNMO. These results are in agreement with the ex situ measurement reported in the Figures S2 and S3 and Tables S2 and S3 displayed in the Supplementary Material.

Figure 4: Contour plot representation of an operando NPD measurement of the first cycle of d-LNMO vs. graphite cylindrical cell: (left) the (222) d-LNMO reflection is plotted, (right) the galvanostatic cycle of d-LNMO vs. Li reference or vs. graphite.

The structural changes observed during charging are mostly reversible during discharging. After the first cycle, the lattice constant of d-LNMO returns to practically ideally the same value of 8.1593(5) Å as before the cycle: 8.1703(8) Å. However, the lithium content was found to be lower after the first cycle, indicating that some lithium was already consumed, most probably by SEI formation and/or by electrolyte side-reactions⁶.

Evolution of the graphite negative electrode

In a similar manner, we followed the evolution of the (002) reflection of the graphite, which transforms into corresponding strong reflections at close scattering angles of the graphite lithiated derivative phases (Figure 5) in course of cell cycling. During the first charge, the different stages of graphite lithiation (namely, stages 1L, 4L, 3L, 2, and 1) can clearly be distinguished³⁶⁻³⁸, and the crystal structures of the main compounds corresponding to these stages might be effectively well analyzed, especially the main stages: LiC₁₈ (described in Supplementary Material, Figures S9 and S10, and Table S5) LiC₁₂ (stage 2) and LiC₆ (stage 1).

During lithiation (Figure 5), a slight shift of the graphite (002) peak toward lower angles starts when the cell reaches 0.45 V vs. Li⁺/Li (see also the white dashed line marked “1L stage” in the Figure S4, ~2.7 h). This phenomenon corresponds to the transition of the graphite to stage 1L (dissolution of Li in the lattice of graphite progressing while the parent graphite lattice remains still intact), which is complete at about 0.2 V vs. Li⁺/Li (dashed line 2 in Figure 5). The crystal structure of this stage 1L compound may still be adequately described using the model of the structure of graphite, with space group *P*6₃/*mmc*, in agreement with the literature³⁹. A

corresponding associated expansion of the graphite lattice occurs practically exclusively along the c -axis: $(a, c) = (2.4608(2) \text{ \AA}, 6.7660(7) \text{ \AA})$, which means a relative elongation of the c lattice constant by $\sim 0.8\%$ as compared to the graphite before cycling: $(a, c) = (2.4623(2) \text{ \AA}, c=6.7141(7) \text{ \AA})$. Between the lines numbered 2 to 4 in Figure 5, corresponding to the evolution of potential 0.2–0.13 V vs. Li^+/Li , the shift of the (002) peak of the stage 1L (graphite-type lattice) towards lower angles progresses further, along with its gradual weakening (between the lines 2 and 3), and further re-entrance between the lines 3 and 4. At the same time, we observe appearance of a new, slightly different pattern of reflections. The crystal structure model of the slightly expanded graphite lattice (corresponding to the stage 1L) is no longer sufficient to carry out the sensible Rietveld fits. Adding a new crystalline phase of the LiC_{18} compound (stage 3L) to the model allows than for the convincing refinements. At the initial stage – between the lines marked 2 and 3 in Figure 5 (graphite potential vs. Li between 0.1 and 0.16 V), the mass fractions of the stage 1L (lithiated graphite structure) and of the LiC_{18} (stage 3L model compound) are gradually interchanging and the patterns collected exactly close to the middle between the lines 2 and 3, deliver practically identical weight fractions of the two phases. Further on – between the lines marked 3 and 4, a rapid decay of the mass fraction of stage 1L compound down to some residual value that will be preserved throughout the whole charge-discharge cycle, occurs. Also quite remarkable would be to note that the lattice constants of this “Li-saturated” Stage 1L compound remain practically unchanged throughout the whole transition between the stages 1L and 3L. This means that the graphite type lattice may accommodate only a certain amount of Li dissolved in it until transforming it to the higher lithiated derivatives, and the next “stability island”, at least under conditions of the slow charge procedure used in our experiment, corresponds to the “stage 3L” compound.^{25, 40} An important note we would like to add to this particular state of the lithiation of the graphite is that, under these rather slow cycling conditions, we have managed to localize the state of the cell where the crystal structure of the phase 3L could be verified with no doubts, since it was producing a dominating contribution to the diffracted intensity during a rather long time (~ 2 hours). In contrast to the previously reported crystal structure model for the stage 3L ($P6/mmm$ space group³⁹), in which the carbon atoms in all layers are located one above another, we could now unambiguously determine its crystal structure to be slightly different. The unit cell dimensions are identical to the previously reported hexagonal model, $a \approx \sqrt{3} \cdot a_c$, $c \approx \frac{3}{2} \cdot c_c$, where a_c, c_c are the lattice constants of graphite. Thus, the structure also contains three distinct layers of carbon atoms, and correspondingly, three interlayer spaces. In the new model, there are two neighboring identically stacked carbon layers (and they form the host place for the insertion of lithium atoms), while the third layer is shifted in a graphite manner with respect to these two. As a consequence, each carbon-carbon interlayer with identical location of atoms in the carbon layers “above” and “below” it, is followed in this stacking by the two interlayer spaces which are organized in a pure graphite manner, namely half of the carbon atoms in these pairs of carbon layers are located one

above another, while another half – above the middles of the carbon hexagons. This new model for the crystal structure of the stage 3L may adequately be described with the space group $P-62m$ (refined lattice constants are: $a = b = 4.272(3)$ Å and $c = 10.526(4)$ Å). An example of the Rietveld refinement based on a pattern representing this particular stage, where the LiC_{18} phase represents the dominating anode material, is given in the Figure S9. An illustration of the newly determined model of the crystal structure of the LiC_{18} phase is given in Figure S10, and the refined crystal structure parameters thereof in Table S5. The transition from stage 3L to stage 2 occurs between the lines numbered 4 and 5 (Figure 5) (respectively between 0.13 V and 0.1 V vs. Li^+/Li). A principal change in the ordering of Li atoms in the host graphite matrix is that, at this stage each second C-C interlayer begins to be host for lithium atoms, these host interlayers being interleaved with the Li-free interlayers. This ordering of Li occupied sites and vacancies in the stage 2 compound (structure of the LiC_{12} type) is best modeled with a lattice with space group $P6/mmm$. The lattice parameters a and c of the LiC_{12} phase are gradually increasing from 4.2767(7) Å, 7.028(2) Å at the beginning of its existence in the charge process to 4.2891(3) Å, 7.0379(6) Å in the fully charged state of a cell (when this phase is then co-existing also with the stage 1 phase with the maximal Li content). Thus, the expansion of the graphite host matrix in the stage 2 compound, compared to the original Li-free graphite prior to cycling, in the direction normal to the carbon sheets, amounts to 4.7-4.8 %, in agreement with the work of Billaud et al.³⁸. As previously reported, the transition from 3L $\rightarrow$ 2 occurs in a two-phase reaction³⁹, i.e. gradual full disappearance of a phase 3L to the benefit of a new phase 2. The appearance of stage 1 begins, after 20 h of charging, at about 75 mV vs. Li^+/Li (~620 mAh) with the following lattice parameters: $a = 4.3150(2)$ Å and $c = 3.6994(3)$ Å (space group $P6/mmm$, and these refined lattice constants correspond to the fully charged state). This last transition, which is known to be kinetically limited, is responsible for a more significant unit cell expansion (~5.1% and ~0.6% along the c - and a -axes, respectively as compared to the LiC_{12} phase in the fully charged state)³⁷. The total volumetric change between Li-free graphite and the stage 1 compound with a stoichiometry close to LiC_6 amounts ~12.8%, and it mainly occurs along the c -axis. As expected from the electroactive material balancing of the cell, the LiC_{12} reflections do not fully disappear at the end of lithiation. Another consequence of this balancing is the presence of stage 1L after step 3, and thus until the end of the charge. At the end of the first charge, the lithium in the cell available for cycling was found to be somewhat higher than 92%. This value indicates that ~8% of the lithium ions extracted from the d-LNMO did not participate in the graphite lithiation process but were most probably “lost” into surface reactions (mainly SEI formation). These results obtained from the operando measurement are in agreement with the results of Rietveld refinements performed on ex situ samples (Supplementary Material, Figure S5 and Table S4).

All phase transitions detected during operando measurements are reversible during the subsequent discharge (Figure 5).

Figure 5: Contour plot representation of an operando NPD measurement of the first cycle of a d-LNMO vs. graphite cylindrical cell: (left) the (002) graphite reflection is plotted which turns into the (003) of the LiC_{18} (between the lines denoted 3 and 4, so called stage 3L), then to the (002) of LiC_{12} and finally to the (001) of the LiC_6 compounds in course of the lithiation; (right) the galvanostatic cycle of graphite vs Li ref or d-LNMO.

In summary, the new cell design developed especially for operando neutron diffraction allowed us to follow the structural changes occurring in the d-LNMO vs. graphite cell. According to our refinement results, ~8% of lithium atoms extracted from the cathode material are being “lost” in the first charge-discharge cycle, which generally is in accordance with the strong fading in the very first cycle, as reported in Figure 2. We have further studied the implications of continuous cycling of the battery by doing a similar neutron diffraction experiment after 100 cycles.

Operando neutron diffraction performed after 100 cycles

Figure 6 shows the evolution of the capacity of the d-LNMO vs. graphite couple in our cylindrical cell. The first 60 cycles were performed at a rate of C/10, and then followed by 40 cycles at a rate of C/2. In the first cycle, a capacity of ~729 mAh was recorded on charge and 602 mAh only upon the discharge. After 100 cycles, only ~60% (~365 mAh) of the initial discharge capacity is reversibly reached.

Figure 6: Capacity evolution of d-LNMO vs. graphite in our cylindrical cell. The fluctuations observed at C/2 are caused by the temperature fluctuations occurring in the room.

The 100th cycle was characterized using operando neutron diffraction in order to gain knowledge on possible ageing mechanisms occurring in a 5 V Li-ion cell. The selected d-LNMO and graphite peaks are presented in Figures 7 and 8, respectively. The slight difference in quality between the pattern collected during the first and the 100th cycle is caused by: i) the faster rate (C/7) used for the neutron diffraction measurement instead of the C/20 rate (for the first cycle), ii) the use of non-deuterated electrolyte, and, iii) the use of a polymeric separator instead of the composite one. For sake of clarity, the Rietveld refinements of the neutron patterns of the discharged cylindrical cell after 100 cycles (charged and discharged state) and after 101 cycles can be found in the Supplementary Material (Figure S6, S7 and S8).

The main difference after 100 cycles (Figure 7) is that the d-LNMO peak in the discharged state (0–2 h range) is found at around 37.37°, rather than at 37.17° (first cycle value, see Figure 3). The refined lattice constant of the d-LNMO phase, 8.1128 (5) Å, can be associated with a lithium content of approximately ~69(4)%. This indicates that ~25% of the lithium disappears from the positive electrode. As soon as delithiation starts, the peak shifts to higher angles until reaching the phase 2 (~5 h) and then, the two-phase reaction occurs with the appearance of phase 3 (refined $a=8.0067$ (6) Å). At the end of charge, a potentiostatic step was applied at 4.9 V vs. Li⁺/Li ~10 h) to ensure full delithiation of the d-LNMO. These transitions are observed on the reverse branch of the cycle during the discharge, but, even with a potentiostatic step at 3.6 V vs. Li⁺/Li, the d-LNMO phase cannot be fully lithiated. The lattice constant of the lithiated d-LNMO amounts to 8.1454 (15) Å, thus corresponding to a lithium content of the fully lithiated d-LNMO of about 74(4)%.

Figure 7: Contour plot representation of an operando NPD measurement of the 100th cycle of d-LNMO vs. graphite: (left) the (222) d-LNMO reflection is plotted, (right) the galvanostatic cycle of d-LNMO vs. graphite.

Similarly, the lithiation of graphite was followed after 100 cycles (Figure 8) and was found to follow the same trend as observed during the first cycle (Figure 5). However, only a very little proportion of stage 1 ($a = b = 4.312(1)$ Å and $c = 3.703(2)$ Å) Li-graphite derivative with composition close to LiC_6 is detected at around 23.25° at the end of the charge process. Our refinement, shown in Figure S7, indicates that, at the end of the charge process the materials' weight proportions on the anode side are: the Stage 1L lithiated graphite: 12 (2) %, LiC_{12} : 77 (3) %, LiC_6 : 11 (3) % phases are present, meaning that only 56(3)% of the graphite was fully lithiated. The phase transitions on discharge are reversible, and graphite returns to its pristine state.

Figure 8: Contour plot representation of an operando NPD measurement of the 100th cycle of d-LNMO vs. graphite cylindrical cell: (left) the (002) graphite reflection is plotted, (right) the galvanostatic cycle of d-LNMO vs. graphite.

Our findings indicate that after 100 cycles a large amount of lithium is missing in the d-LNMO electrode. Two hypotheses are postulated to explain such behavior: i) the lithium is no longer available to participate in the electrochemical processes (most probably consumed by side reactions), and ii) the electroactive materials were damaged structurally and cannot accept lithium anymore.

To verify which hypothesis was correct, d-LNMO and graphite electrodes were first cycled in full-cell configuration (1C rate) until losing ~30% of their initial capacity. Then, one of the electrodes was extracted and replaced by metallic lithium (half-cell configuration) with changing neither the separator nor the electrolyte. After 100 cycles at a rate of 1C in a full-cell configuration (Figure 9), only 70% of the initial specific charge is obtained. Then, once the cells are disassembled and cycled in a half-cell configuration, we can see that the electroactive materials (d-LNMO or graphite) recover their initial specific charge (almost 100% at a rate of C/10) even after long-term cycling (additional 150 cycles). These results confirm that the materials are neither structurally damaged nor the electrode lost integrity and consequently contact. Hence the hypothesis number 1 regarding the gradual loss of lithium from the active charge-discharge processes upon multiple (100x) cycling in the full-cell configuration is confirmed.

Figure 9: Specific charge of d-LNMO vs. graphite full and then half-cell configuration (coin cell like design) at a rate of 1C.

Conclusions

A new cylindrical cell design was developed to investigate during cycling the behavior of d-LNMO vs. graphite cells using operando neutron diffraction. This new cell has reliable electrochemistry, even with highly loaded electrodes, and allows carrying out Rietveld refinements on the operando measurement data. The cell can be cycled at slow and fast rates, and can be used to study ageing mechanisms since it sustains long-term cycling. Through careful design, the cell can achieve a better signal-to-noise ratio than a typical commercial cylindrical cell. During operando measurements, the lithium content in the different host materials could be determined and correlated to the electrochemical performance, notably allowing an estimation of the lithium consumption in side-reactions (SEI/SPI formation). Following this approach, we found out that, after long-term cycling (100 cycles) about one third part of the lithium was consumed in side reaction(s) and that the materials from positive and negative electrode were not structurally damaged. This new methodology allows a better understanding of the fading mechanisms occurring in d-LNMO vs. graphite Li-ion batteries.

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Supporting Information.

The comparison between the neutron pattern of a commercial cell and our new developed neutron cell. Complete set of results from the Rietveld refinements of the ex situ and in situ measurements for the d-LNMO pristine powder, half and fully charged d-LNMO electrodes, and fully charged graphite electrode after the 1st cycle and 100th cycle. The structure of LiC₁₈ graphite electrode. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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