PAPER

Charge/discharge cycling of Li$_{1+x}$(Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$)$_{1-x}$O$_2$ primary particles performed in a liquid microcell for transmission electron microscopy studies

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Abstract

Ni-rich layered oxides are promising positive electrodes for fulfillment of government and industry targets for lithium-ion-battery-operated electric mobility purposes. Apart from ongoing research focusing on their design and material production, advanced characterization techniques can provide valuable insights on their stabilization by monitoring in situ the degradation mechanisms. Herein, we use liquid-phase transmission electron microscopy to examine the effects of electrochemical stimuli on Ni-rich oxide cathodes by introducing an optimized micro-scale battery configuration. Ball-milled Li$_{1+x}$(Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$)$_{1-x}$O$_2$ (NCM622) particles were cycled against a delithiated LiFePO$_4$ anode and the effects of different cycling methods were investigated. We show that commonly used cyclic voltammetry measurements at high scan rates cannot be used to simulate battery operation in situ due to geometry limitations of the cell that inhibits Li ion transport. However, using galvanostatic charge/discharge cycling and introducing a pause every 10 cycles for a total of 50 cycles results in degradation in the form of Mn and Co ion dissolution from the first 20 nm of the surface. Our results suggest that although performing battery cycling using liquid cell electron microscopy may differ from the case of coin cells, by tuning the electrochemical profiles used similar degradation mechanisms can be attained.

1. Introduction

Lithium-ion-battery-powered devices are indispensable for everyday use. As efficient as this technology has been, there is still space for improvements toward capacity retention, energy level, lifetime, and safety. In particular, ongoing research in optimization of layered cathode materials for electric automotive applications focuses on achieving sufficient energy density without compromising on capacity during high voltage operation over numerous cycles. John Goodenough was the first to propose layered structures based on transition metal (TM) oxides that displayed significant improvement in the reversible mobility of lithium ions [1]. Even though the initially implemented Co-rich cathodes never quite reached the theoretical specific capacity, the underlying layered structure was optimal for use in lithium ion batteries since it provides an independent channel for lithium ion transportation during battery charge and discharge [2, 3].

Among the layered oxide cathodes, Ni-rich cathodes have attracted a lot of research [4, 5]. Specifically, Li$_{1+x}$(Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$)$_{1-x}$O$_2$ (NCM622) is currently being used as the cathode material in electric vehicles due to its high capacity (180 mAh/g), high galvanic potential (4.6 V) and its reduced fraction of the costly

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and toxic element cobalt [6, 7]. A high Ni content is important to achieve high reversible capacity, Co improves the layered ordering as well as rate capacity, whilst Mn enhances the structural and thermal stability [8]. However, the increased Ni content can negatively affect the capacity retention observed by the evolution of the layered structure, which is initially established by Co, into other less transport efficient structures such as spinel or rock salt [9–12]. Several studies have reported that the degradation of Ni-rich cathodes is a result of elemental migration and redox reaction of the transition metal ions that eventually leads to structural changes during cycling [10, 13–17]. To improve the durability of lithium ion batteries comprised of layered cathodes, several methods that depress the parasitic reactions and compensate for the instability of transition metal ions during cycling have been proposed such as surface modification leading to cathode materials with core–shell structure and gradient-concentration particles [12, 18]. For conventional usage of this material, the cathode electrode active material is composed of almost-spherical secondary particles of about 10 μm in diameter. They are formed from self-bounded primary particles of several hundreds of nanometers. The layered structure of NCM (R3m) promotes Li de-/intercalation, however, during cycling structural and chemical degradation of the particles limits their lifetime. Previous studies for similar structures after charge/discharge cycling at moderate voltages revealed intergranular cracking using SEM [19, 20]. When the voltage increases, the structural degradation of the surface of some outermost grains becomes dominant due to lattice oxygen release from the near-surface regions of the primary particles and hopping of the transition metals into the Li sites, before being finally relaxed to a different crystal structure (spinel and/or monoclinic), as revealed by TEM studies [21]. It is this rearrangement or leaching of transition metals that ultimately blocks the Li pathway. Despite insights gained thus far by ex situ nanoscale probing of pristine and cycled cathodes, real-time observations of the compositional and structural changes during electrochemical reactions of Ni-rich cathode materials can shed valuable light to the ageing processes taking place.

In situ liquid-phase, electrochemical TEM for lithium-ion battery applications was first implemented about 20 years ago and was pioneered by Frances Ross [22]. Her early work involved electrochemical Li nucleation, growth and dendrite formation where she monitored the processes taking place during battery cycling by observing growth at the edge of the working electrode [23]. More in situ studies on batteries have emerged recently that were able to determine the lithiation states of LiFePO4 (LFP) particles within a functional electrode [24], thus probing the chemistry during battery operation [25], and to in situ monitor electrolyte degradation in the solution by TEM [26]. However, monitoring real-time degradation mechanisms of NCM622 has not been possible due to the restrictions imposed by the large particle size. In addition, the system used for liquid cell observations does not emulate well the real battery system (cathode, additives, binders, electrolytes, reference electrode and anode) and no direct comparison with a standard battery setup such as a coin cell has previously been reported.

Herein, we demonstrate that battery cycling of NCM-based materials in conventional liquid TEM microcells is feasible. Specifically, the electrode configuration inside the liquid cell system was designed and optimized for the cycling of primary NCM622 particles and it was found to conform well with the expected bulk electrochemical measurements. We describe the utilization of LFP particles as non-gassing counter electrode which does not contaminate the electrolyte and which can be used as a pseudo-reference electrode. Cyclic voltammetry (CV) and galvanostatic charge/discharge electrochemical analysis were performed to evaluate the capacity decay of the cathode material during cycling. The results confirm that NCM cycling can be performed in the liquid cell over 50 cycles with reasonable coulombic efficiency and capacity retention of ~ 65%, which is realistic for such a cell.

2. Methods

2.1. Particle size modification of NCM622

Li1+x(Ni0.6Co0.2Mn0.2)1−xO2 powder, simplified as NCM622 in the following, was provided as secondary particles (BASF, Germany). To decrease the particle size so that they fit within the restricted volume of the liquid cell and are electron transparent, a three-step wet ball milling method using N-methyl pyrrolidone (NMP, anhydrous, 99.5%, Sigma-Aldrich) as the solvent was introduced. Milling was performed using a ZrO2 beaker with ZrO2 beads of varying sizes with a Fritsch pulverisette 7 ball-mill (Fritsch, Germany). The milling details are summarized in table 1. The crushed powder was annealed with a ramp rate of 10 °C min−1 up to 600 °C and it was then placed on hold for 1 h before free-cooling to room temperature in order to recrystallize the particles. Specific area measurements were used to track the size of NCM622 particles after each milling step. The specific surface area (SSA) of the particles was measured using the Brunauer−Emmett−Teller (BET) method by an Autosorb iQ nitrogen gas sorption analyzer (Quantachrome Instruments, USA). Micrographs of secondary and ball milled primary particles were also taken with a scanning electron microscope (Zeiss Merlin) for checking the morphology change after processing. Due to the increasing specific surface area of the ball-milled NCM622 particles, the proportion of binders and
additives was increased to stabilize the particles that were placed onto the current collector. To perform coin cell electrochemical measurements of the crushed particles, the binders and additives were added by performing an additional ball-milling step at low rotation speed to homogeneously distribute all the materials. However, for the liquid cell experiments, the recrystallized crushed powder was simply mixed with the binders and additives, without any additional mechanical force (see section 2.3 for details).

### 2.2. Chip optimization for the chip-based micro-battery system

Typically, two microelectromechanical-based (MEMS) chips are used to seal the fluid for liquid cell electron microscopy studies: a top chip that is specially patterned with microelectrodes and a bottom chip that acts as a spacer that determines the thickness/volume of the liquid layer. For the battery studies herein, the top chip was microfabricated in-house and was patterned with three electrodes, namely two Pt (working and counter) and one Au (reference) on a Si substrate deposited with a 50 nm SiN$_x$ membrane. The chip was back-etched to expose an electron transparent membrane region (the window) to allow experiments in transmission mode. The working electrode ($5.85 \times 10^5$ $\mu$m$^2$) was patterned on the membrane window, and the counter electrode was designed to have a larger surface area ($7.625 \times 10^5$ $\mu$m$^2$). Platinum electrodes were used as stable current collectors due to the ability of Pt to transfer electrons without any risk for corrosion of the electrode within the examined potential range during the measurements. The requirements for the counter electrode concern adequate lithium hosting during NCM622 delithiation, whereas the reference electrode needs to remain stable during cycling. To this end, LFP particles were dropcast onto the counter electrode strip using a micromanipulator where they served as lithium host and as a pseudo-reference electrode. The delithiation of LFP was achieved by lithiating the blank Au electrode before cycling the NCM material (vs. LFP), where the Li$_x$Au alloy [27] could form without much volume expansion or thickness extension. Due to the restricted volume of the Au layer, however, we expect major portions of the lithium being deposited in its metallic state rather than as Au-Li alloy, so that a well-defined reference potential for the LFP during delithiation can be obtained. More than 50 reproducible cyclic voltammograms and galvanostatic charge/discharge cycles were achieved with this setup.

### 2.3. Electrode preparation

For the working electrode, either pristine or ball-milled NCM622 primary particles (after milling step 3) were used as cathode active material for coin cell testing. The electrode was prepared by dispersing the particles (96%wt for pristine NCM or 80%wt for ball-milled NCM), conductive carbon (Super C65, Timcal, Switzerland) (2%wt or 10%wt), and polyvinylidene fluoride binder (PVDF, Kynar HSV 900, Arkema, France) (2%wt or 10%wt) in NMP. The NCM622 slurry was mixed in a planetary mixer (Thinky, USA). The slurry of primary NCM622 particles was mixed with 10 mm ZrO$_2$ grinding balls in the planetary ball-mill in order to avoid the agglomeration and enhance the dispersion of components. A 30 $\mu$m 4-edge blade in an automated coater (RK PrintCoat Instruments, UK) was used for spreading the slurry on Al foil (18 $\mu$m, 99%, MTI, USA). It was dried at 50 °C and the final loading was 0.167 mg cm$^{-2}$. Electrodes with a diameter of 14 mm were punched and dried overnight at 120 °C under dynamic vacuum in a glass oven (drying oven 585, Büchi, Switzerland) and they were then transferred to an inert gas glovebox (O$_2$ and H$_2$O < 0.1 ppm, MBraun, Germany) without exposure to ambient air. Metallic lithium discs (450 $\mu$m, 99.9%, Rockwood Lithium, USA) with 15 mm diameter were used as counter/reference electrode in the coin cell. For the in situ studies, the counter/reference electrode consisted of 90 wt% LiFePO$_4$ (LFP, Umicore) particles and 10 wt% of PVDF.

The diluted suspension (6 mg ml$^{-1}$) of both slurries in NMP was sonicated for 30 min prior to filtering with 1 $\mu$m pore size paper. The filtered suspension was sonicated for 10 min before dropcasting the suspensions onto the current collector strips. The suspension was then taken with a capillary (Narishige GD-C 1, Tokyo, Japan) pulled by a micropipette puller (Narishige PC-10, Tokyo, Japan), and dropcast on the selected electrode (NCM on the working and LFP on the counter electrode) using a micromanipulator (Narishige MMO-4 hydraulic micromanipulator combined with a mechanical coarse manipulator).

### Table 1. The procedure of three-step ball-milling of NCM622 particles.

| Step | Milling balls (mm) | Material to solvent ratio by weight | Speed (rpm) | Time (min) | Rest (min) | Repeat | SSA ($m^2 g^{-1}$) |
|------|--------------------|----------------------------------|-------------|------------|-----------|--------|-------------------|
| 1    | 10                 | 1:1.5                            | 400         | 5          | 15        | 6      | N.A.              |
| 2    | 3                  | 1:1.5                            | 800         | 2          | 18        | 6      | 3.257             |
| 3    | 1                  | 1:3                              | 1000        | 3          | 17        | 32     | 14.991            |

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prepared chip was dried on a hot-plate at 60 °C in an Ar filled glovebox for 12 h to fully remove NMP without damaging the electrochemical chip.

2.4. Micro-battery assembly within liquid cell
Prior to assembling the chips onto the TEM holder (Hummingbird Scientific, Lacey, WA, USA) [28], both top and bottom (spacer thickness was 1 µm) chips were treated with air plasma for 90 sec at 100 W to enhance the wettability of the electrolyte with the surfaces of the three electrodes. The holder was then transferred into the glovebox for degassing. Ar gas was purged through the microfluidic tube to remove the trapped gas from the micro-cell. The holder was kept in Ar environment for 3 h before introducing the electrolyte (1 M LiPF$_6$ in 3:7 ethylene carbonate (EC): ethyl methyl carbonate (EMC), BASF, <20 ppm water). Wetting of the electrodes was confirmed by a stable open circuit voltage (OCV) reading on the connected potentiostat (SP-300, BioLogic, France) once the electrolyte was introduced into the liquid cell through microfluidic tubes.

2.5. Electrochemical measurements
The coin cell was assembled using the method described in detail previously [29], with both pristine and ball-milled NCM622 as the cathode. Both coin cells were cycled at C/5 between 3 V and 4.6 V (vs Li/Li$^+$) for 10 cycles. For liquid cell measurements, the amount of electrode material loaded onto the chip by dropcasting was difficult to quantify (roughly a few hundred pH NCM on the working electrode). Therefore, galvanostatic charge/discharge measurements were conducted at an experimentally selected current of 50 nA between −1 V and +1.5 V vs. LFP (resulting in +2.5 to +5 V vs Li/Li$^+$ assuming the LFP potential of roughly 3.5 V vs Li/Li$^+$ in this current range). Additionally, a higher upper cutoff potential was applied for galvanostatic charge/discharge compared to the potential set for cyclic voltammetry (1.4 V vs. LFP) to compensate for the high overpotential involved in the liquid cell system under constant current cycling conditions. Cyclic voltammetry (CV) with a rather fast scan rate of 20 mV s$^{-1}$ was also performed. This accelerated ageing test method was initially chosen to facilitate the degradation observations with in situ characterization by TEM, which is generally limited by the experimental time [30–32].

Before using loaded LFP as counter/reference, pre-delithiation needed to be conducted for driving the LFP into the stage of charge (SOC) where it is able to hold a stable potential over a wide range of lithiation/delithiation during cycling of the NCM working electrode [33]. The LFP loaded Pt electrode was connected as working electrode, while the blank Au was connected as counter and reference. 500 nA current was applied to initialize the delithiation of the LFP and the current was decreased step by step until the potential of LFP vs. lithiated gold started to deviate from the stable potential of delithiated LFP vs. Li/Li$^+$. NCM was then connected as working electrode while delithiated LFP was connected as counter (and reference) for in situ cycling.

In order to measure the electrochemical performance of the cathode of the micro-battery assembled in the liquid cell, CV was firstly used to confirm the stability and reproducibility of the experiments. Then, galvanostatic charge/discharge was carried for tracking the reversibility of the reaction during cycling and the subsequent capacity decay. A low current of 50 nA was typically used for in situ liquid electrochemical experiments due to the otherwise too large ohmic losses of the setup. Additionally, as relatively longer cycling time was consumed for one cycle while applying such a low constant current, this is considered as a milder way of cathode cycling compared to CV and therefore the mass transport of lithium ions of electrolyte could be well regulated under these conditions.

2.6. Post mortem electron microscopy
After cycling in the liquid cell holder, the chip was unmounted and rinsed with dimethyl carbonate (DMC) to remove the electrolyte residues. The chip was kept sealed within an Ar filled vial during the transfer between the glovebox and the microscopes. A ThermoFisher Scientific Talos F200X TEM operated at 200 kV was used to examine the top chip. Scanning TEM (STEM) and energy dispersive spectroscopy (EDS) were used to identify structural and compositional changes, respectively, after the electrochemical operation. The loading time was kept short to minimize exposure of the samples to air.

3. Results and discussion

3.1. Bulk electrochemical response of ball-milled primary particles
The average size of the secondary NCM particles is in the micrometer scale (figure 1(a)), which makes it impossible to load in the liquid cell for electron microscopy studies. Therefore, a procedure for retrieving the primary particles from the secondary particles was introduced. A three-step ball-milling method was undertaken to produce particle sizes of 200–300 nm (figure 1(b)), which was followed by annealing to
recrystallize the particles. To confirm the electrochemical performance of the ball-milled particles as cathode electrodes, coin cell cycling of the secondary and ball-milled particles was first performed. Figure 1(c) depicts the differential capacity of the ball-milled and pristine particles as a function of the working electrode voltage vs. Li/Li$^+$. The good alignment of the differential capacity peaks for both materials indicates that the same redox reactions during cycling take place at 3.7–3.8 V vs. Li/Li$^+$. Compared to the pristine NCM622 (figure 1(d)) the initial specific capacity of the ball-milled NCM622 sample (figure 1(e)) has decreased by 40% (i.e. drop from 200 mAh g$^{-1}$ to 120 mAh g$^{-1}$). This capacity loss of the ball-milled NCM622 could be linked to the interaction between the surface of the electrolyte material with the electrolyte as a result of the \( \approx 50 \)-fold larger exposed surface area of the ball-milled NCM622 particles (from 0.3 m$^2$ g$^{-1}$ in the case of the pristine NCM622 to 15 m$^2$ g$^{-1}$ for the ball-milled material). In addition, the capacity loss of the crushed particles for the coin cell measurements could be due to possible structural damage during the slurry preparation with the participation of grinding balls. The layered structure of the crushed particles after annealing was confirmed by high resolution TEM (HRTEM) in figure 1(f), where the periodicity of the fringes matches the spacing of the layers 0.47 nm [21] and the fast Fourier transform (FFT) (figure 1(h)) on the edge of the particle is consistent with R$3m$ rhombohedral crystal structure from [11 0] zone axis. In contrast, HRTEM and the corresponding FFT on the selective regions of grinded particles after slurry preparation for coin cell measurements (figure 1(g)) shows that the structure is damaged and is partially transformed into spinel (Fd$3m$) close to the surface of the particle. However, it is noted that this final preparation step was specifically performed for coin cell measurements and it was not involved in the electrode suspension preparation for dropcasting on the electrochemical chip for \textit{in situ} TEM. Therefore, the electrochemical measurements of the ball-milled NCM622 particles used as working electrode for the experiments with the \textit{in situ} TEM cell are expected to represent well the properties of the pristine NCM622 material making the electrochemical measurements with the two different cell setups comparable.

3.2. Electrochemical response of ball-milled primary particles on the electrochemical chip

The cycling performance of ball-milled NCM particles was first tested in the confined electrochemical configuration of the liquid cell. The SEM images in figures 2(a) and (b) indicate the microfabricated coplanar electrode geometry of the top electrochemical chip. The geometry of the working and counter electrodes allows to site-specifically deposit the ball-milled NCM622 particles and LiFePO$_4$ nanoparticles on the respective electrodes. After control experiments, a two-electrode configuration was found to provide interpretable electrochemical profiles, hence the third electrode, normally used as a reference, was left unloaded. Prior to the cycling experiments of the NCM622 particles, the LFP particles were pre-delithiated by electrochemically transferring the lithium ions onto the Au reference electrode strip of the cell (labeled RE in figure 2(a)). This preparation of the counter electrode serves to utilize it as simultaneous pseudo-reference electrode (i.e. as electrode which retains an essentially constant potential so that its potential serves as pseudo-reference potential). To initiate the nucleation of metallic lithium on the Au reference electrode strip during delithiation of the LFP, a current of 500 nA was firstly applied and then reduced step-wise until the stable potential plateau of LFP was observed, as shown in figure 2(c). The potential reading between the partially delithiated LFP and the lithiated Au stabilized at the value closer to the theoretical value of delithiated LFP vs. Li$_x$Au alloy (3.5 V) while applying lower current densities (from 500 nA down to 5 nA). After this partial delithiation of the LFP deposited on the counter electrode strip, galvanostatic charge/discharge cycling was performed in the liquid cell inside the glovebox to confirm the electrochemical performance of the system. Cycling with a constant current of 50 nA shows reasonable electrochemical performance of the ball-milled NCM622 particles (figure 2(d)). Interestingly, the coulombic efficiency of this setup is close to 100% after a few cycles, which indicates good reversibility of the charge/discharge reaction in the liquid cell configuration, reasonably close to the expected behavior for a conventional cell setup. Moreover, the initial discharge capacity and the capacity fading of the ball-milled NCM622 particles obtained in the liquid cell setup was found to be quite comparable with the corresponding values obtained in the coin cell configuration (see figure 1(e)), having around 80% capacity remaining after 10 cycles.

3.3. Cycling of ball-milled particles with varying electrochemical input in a liquid microcell TEM holder and post mortem TEM analysis

Local chemical transformations of the ball-milled particles were evaluated \textit{in situ} by applying a range of electrochemical conditions. The electrochemical stimuli performed in the liquid cell TEM holder and the post mortem STEM-EDS analysis of the NCM particles participating in the reactions are displayed in figure 3. The particles' response to cyclic voltammetry was first investigated (figure 3(a)). Compared to reported CV curves from coin cell experiments, broadening of the redox peak in the CV within the liquid cell is seen. This is attributed to geometric differences between the two configurations. It is known that the liquid TEM...
Figure 1. SEM micrographs of the pristine (a) and the ball-milled (b) NCM622 particles. The electrochemical performance characteristics of the pristine and of the ball-milled NCM622 particles obtained in conventional coin cells are shown in the following: (c) differential capacity vs. potential plot for the pristine NCM622 (blue) and the ball-milled NCM622 first (red) and third (black) cycle at C/5 charge/discharge between 3 V and 4.6 V vs. Li/Li$^+$. The working electrode potential vs. specific NCM622 capacity for 10 galvanostatic charge/discharge cycles between 3–4.6 V is shown for pristine NCM622 (d) and for the ball-milled NCM622 particles (e). (f) HRTEM micrograph of the annealed particles and (g) HRTEM micrograph of the primary particles after grinding-assisted slurry preparation. (h) FFT of regions indicated as yellow squares in (f) and (g) with the corresponding numbers. Scale bar is 5 nm$^{-1}$.

cell causes deviations from the ideal Nernstian behavior and exhibits increased ohmic drop [24, 28, 34, 35]. Moreover, geometry dependent mass transport and diffusion variation in the microband/microfluidic system will impact the electrochemical measurement and also result in peak broadening [36]. The particles did not exhibit significant compositional modification after 5 cycles and the structure remained intact, as revealed by the atomic ratio of Ni, Co and Mn that remained at 3:1:1 over the whole particle (figure 3(b) and (c)). Typically, the high scan speed during CV analysis does not provide sufficient time for lithium ion transport towards the electrode. Such CV conditions are inadequately used in liquid cell TEM testing of
battery systems and cannot be directly compared to galvanostatic battery cycling. Next, charge/discharge measurements were performed. Particles mapped in figure 3(e) were cycled 50 times with a constant current of 50 nA with one hour rest every 10 cycles (figure 3(d)). They exhibit Mn and Co dissolution up to 20 nm from the surface as indicated by the arrow in the line profile of atomic fraction in figure 3(f). The dissolution of Mn and Co ions from the NCM particles after cycling is caused by the ionic disorder that takes place along with the de-/intercalation process consisting of ionic diffusion within the electrolyte and solid-state diffusion of lithium atoms within the electrode materials [37, 38]. The pause introduced between the cycles ceases the polarization via minimization of the adsorbed ions on the surface of the electrode, which is reflected in the observed bounce back and destabilization of the charge capacity from the first cycle after each pause, as depicted in figure 3(d). Suspending the polarization on the electrode not only triggers the relaxation of ions within the double layer by electrolyte ionic concentration gradient redistribution but also assists on the rearrangement of the lithium atoms through solid-state diffusion within the NCM particles. As reported previously, the ionic radius of Ni^{2+} (0.69 Å) is similar to Li^{+} (0.76 Å) and has lower diffusion barrier, making it more feasible for Ni/Li exchange and Ni rearranging within the NCM material while the Mn and Co ions tend to undergo irreversible chemical reaction with the liquid electrolyte that, together with the electrochemical redox, leads to their dissolution from the surface of the particles after cycling [39, 40]. The rest between several cycles provides the opportunity for element relaxation from the disordering induced by the lithium de-/intercalation during charge and discharge cycling and it should serve as the means to perform reproducible battery cycling experiments using liquid-phase electron microscopy.
4. Conclusion

In summary, a versatile setup for micro-battery TEM experiments in liquid electrolytes was assembled and it was found practical for a range of electrochemical measurements pertinent to lithium ion battery testing. The electrochemical performance of ball-milled NCM622 primary particles was shown to be representative of the secondary ones that are commonly used in bulk systems. Therefore, the mass transfer limitation and internal resistance caused by the relatively smaller volume of the electrolyte and the restrictions imposed by the quantity of the electrode active material that can be loaded on the microelectrodes do not inhibit the experimental measurements. However, the electrochemical measurements revealed that the geometry-related limitations of the in situ TEM setup can affect the lithium de-/intercalation within the Ni-rich layered oxide cathodes which drive the migration of transition metal ions. In this study, we showed that by adding pause conditions during galvanostatic charge/discharge cycling, the micro-system's electrochemical behavior leads to cathode degradation mechanisms comparable to the expected ones in bulk cells. Thus, with the methodology developed herein, we are now close to monitoring in real-time the complex degradation
processes involved in the positive electrodes of lithium ion batteries and directly relate them with the electrochemical conditions applied for their ageing.

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