Surface/Interface Study on Full $x\text{Li}_2\text{MnO}_3 \times (1 - x)\text{LiMO}_2$ ($M = \text{Ni}, \text{Mn}, \text{Co}$)/Graphite Cells

Lucien Boulet-Roblin, Mario El Kazzi, Petr Novak, Claire Villevieille

► To cite this version:

Lucien Boulet-Roblin, Mario El Kazzi, Petr Novak, Claire Villevieille. Surface/Interface Study on Full $x\text{Li}_2\text{MnO}_3 \times (1 - x)\text{LiMO}_2$ ($M = \text{Ni}, \text{Mn}, \text{Co}$)/Graphite Cells. Journal of The Electrochemical Society, 2015, 162 (7), pp.A1297-A1300. 10.1149/2.0491507jes . hal-02626074

HAL Id: hal-02626074

<https://hal.science/hal-02626074>

Submitted on 26 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Surface/interface study on full $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Ni, Mn, Co}$)/graphite cells**

2 Lucien Boulet-Roblin, Mario El Kazzi, Petr Novák, and Claire Villevieille*

3
4 Electrochemical Energy Storage Section, Paul Scherrer Institute, CH-5232 Villigen PSI,
5 Switzerland

6 * E-mail: claire.villevieille@psi.ch

7
8 **Abstract**

9 We report the behavior of full Li-ion cells with a $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Ni, Mn, Co}$)
10 (hereafter called HE-NCM) cathode and a graphite anode. The cells' cycling behavior,
11 especially with regard to the degradation processes (mainly of the electrolyte) occurring in the
12 5 V region, does not strongly depend on the cycling rate but rather on the calendar time of
13 cycling. At the fast 1 C rate, we demonstrate 250 cycles with more than 80% capacity retention
14 in a standard carbonate electrolyte. A surface analysis combining *post-mortem* scanning
15 electron microscopy (SEM) and X-ray photoemission spectroscopy (XPS) revealed differences
16 in the electrodes' surface composition and morphology, and the suggested explanation for these
17 differences was found in the thickness of the polymer layer developed at the surface of the
18 particles.

19
20 **Keywords:** NCM, graphite, full-cells, XPS, SEM

Introduction

Since the introduction of LiCoO_2 as a positive electrode material in Li-ion batteries, layered metal oxides have drawn significant scientific interest.¹ As cobalt-based materials are both toxic and expensive, there is a need to minimize the amount of cobalt used in electrode materials. Layered low-cobalt oxides with the formula $\text{Li}_x\text{Ni}_a\text{Mn}_b\text{Co}_c\text{O}_2$ (NCM) deliver an experimental specific charge of up to 200 mAh/g while cycling up to 4.8 V vs Li^+/Li .² This high voltage material has been described as having a crystal structure of layered $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ with Li_2MnO_3 domains³, the activation of the latter is believed to account for a long potential plateau at ~ 4.5 V vs. Li^+/Li observed during the first oxidation (delithiation). Structural and interfacial changes have been observed at very positive potentials during both activation and subsequent cycling of this NCM material, and different reaction mechanisms have been proposed to explain the observed oxygen release from the Li_2MnO_3 domains.⁴

The voltage fading that is observed during the cycling of these materials has mainly been explained by the reorganization of the aforementioned Li_2MnO_3 domains, a process which leads to manganese disproportionation and leaching. However, another challenge results from the high voltage cycling window of these materials, in that the standard carbonate-based electrolytes (that would normally be used in devices) tend to decompose above approximately 4.5 V vs. Li^+/Li .⁵ This decomposition in turn results in surface layer formation that can inhibit the practical specific charge of the cells.

Several possible approaches exist to buffer these difficulties. In the case of the Li_2MnO_3 domains, there are reports in the literature suggesting both, substitution of the transition metals and surface coatings as a means to obtain better stability during cycling.^{6,7} On the other hand, the mitigation of the electrolyte decomposition has been achieved through the use of electrolyte additives⁸; in the case of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{C}$ full-cells, the use of succinic anhydride and 1,3-propanesultone led to a capacity retention of 80% after 100 cycles.⁷

Given the significant impact of surface layer formation on cell performance, we therefore decided to couple electrochemical investigations with electrode surface properties, especially with regard to morphology and composition of the polymer surface layer developed during cycling. Full test cells were made using high energy NCM (HE-NCM) and graphite for the cathode and anode, respectively. Cells with both electrodes were cycled at different rates and were further analyzed by scanning electron microscopy (SEM) and X-ray photoemission spectroscopy (XPS) for a better understanding of the impact of current rates.

Materials and methods

Cathode properties—The properties such as X-ray diffraction, neutron diffraction etc... are described elsewhere ⁹

Electrode preparation—Electrodes were prepared by casting a mixture of 80 wt% active material HE-NCM (BASF) or graphite SFG44 (Imerys), 10 wt% Super-P carbon (Imerys), and 10 wt% Kynar Flex binder (Solvay), suspended in N-methyl-2-pyrrolidinone (Fluka), onto aluminum foil (for HE-NCM) or copper foil (for graphite). The casted slurry was dried under vacuum at 80°C overnight. Circular 13 mm diameter electrodes were punched out of the dried cast and then reheated at 120°C under vacuum overnight in order to remove remaining NMP and absorbed water. The thickness of the electrode was slightly more than 80 μm.

Cell assembly—Coin-cells (HE-NCM/C), made of titanium, were assembled from the prepared electrodes in an Ar-filled glove box. Glass fiber separators were used, they were soaked with the electrolyte 1 M LiPF₆ in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 w/w) (Novolyte), called hereafter LP30. The electrode balancing of the full-cells was 1.0:1.2 (C:HE-NCM) in mass and the loading was ~3.6 mg/cm² for the HE-NCM electrode and ~3.0 mg/cm² for the graphite electrode, respectively.

Cell cycling—Electrochemical cycling was carried out galvanostatically between 1.0 V and

4.8 V at C-rates ranging from C/10 to 1-C (assuming theoretical values of 280 mAh/g for HE-NCM and 372 mAh/g for graphite SFG44), using Bat-small from Astrol Electronics AG. All measurements were performed at room temperature in a thermal chamber ($25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$).

Post-mortem characterization—For *post-mortem* surface studies performed both using SEM and XPS, the cells were stopped at the end of the discharge (1.0 V), the HE-NCM and the graphite electrodes were separated from the rest of the battery components, gently washed in a Petri dish containing DMC solvent (to remove electrolyte salt residues not intrinsic to the Solid Permeable Interphase or Solid Electrolyte Interphase layer (SPI/SEI)), and then dried prior to being packed into a hermetically sealed transfer chamber for transfer to the XPS or SEM. All operations were completed in a glove box under Ar atmosphere.

SEM measurements—The analyzes were performed with an Ultra55 (Carl Zeiss).

XPS measurements—XPS measurements were carried out with a VG ESCALAB 220iXL spectrometer (Thermo Fisher Scientific) using focused monochromatized Al K_{α} radiation (1486.6 eV). The spectrometer was calibrated using the Ag 3d_{5/2} peak with a binding energy of 368.3 eV. The samples had an analyzed area of about 500 μm^2 and the analysis chamber had a recorded pressure of approximately 2×10^{-9} mbar. Analysis was completed at a power of 150 W, and the spectra were recorded in constant analyzer energy mode at a pass energy of 30 eV.

Control spectra were recorded at the beginning and at the end of each experiment to check if any degradation of the samples occurred in the spectrometer. The binding energy scale was calibrated using the Super P carbon C1s peak (C-C binding energy of 284.4 eV).

Results and discussion

Figure 1 represents the practical specific charge of HE-NCM/C cells cycled between 4.8 V and 1.0 V in LP30 electrolyte at scan rates of 1 C, C/2, C/5, and C/10. For all tested rates, we notice a significant capacity drop after the first cycle due to the irreversible activation of the Li_2MnO_3 domains¹⁰⁻¹³. Then, starting with the second cycle, we observe two different trends, the first pertaining to the “fast rates” (1 C and C/2) and the second to the “slow rates” (C/5 and C/10). At this point, the practical specific charge is close to 250 mAh/g for the slow rates and close to 200 mAh/g for the fast rates. The difference at this stage between fast and slow rate is attributed to kinetic limitations of the electrodes which explains why the specific charge is lower at fast rate. Regarding the cycling stability for the fast rates, only ca. 10% capacity is “lost” after 100 cycles and ca. 25% capacity after 300 cycles. About half of the useful specific charge is “lost” after 600 cycles for the C/2 rate. For the slower rates, approximately 50% capacity is “lost” for the C/10 rate and less than 40% for the C/5 rate after about 100 cycles. Excluding kinetic effects, these results can be explained by the observation that the electrolyte/electrode interface will stay for significantly longer time in the highly oxidative and therefore the degradative range above 4.5 V vs. Li^+/Li at slower rates than at faster rates as indicated in the inset of the Figure 1. For example, after 1000 hours of cycling, cells at the C/10 rate had only completed about 50 cycles whereas cells at the C/2 rate had completed about 250 cycles. Those results are summarized in the Table 1. The aging of the full-cells that most likely mainly occurs under these highly oxidative conditions leads to greater electrolyte decomposition and, possibly, transition metal dissolution/disproportionation. 10 Thus, looking at the calendar aging of the cells instead of the cycling aging as indicated in the inset of the Figure 1 is also important.

Figure 1. Specific charge with respect to the oxide electrode of full HE-NCM/C cells at C rates of 1 C, C/2, C/5, and C/10 with LP30 electrolyte; inset – Specific charge vs. time for the first 400 h.

Rate	C/10	C/5	C/2	1 C
Specific charge (mAh/g) after 100 cycles	131	165	174	185
% of remaining specific charge after 100 cycles*	52	67	81	94
Specific charge (mAh/g) after 400 h	198	193	161	151
% of remaining specific charge after 400 h*	80	79	75	76

Table 1. Summary of the specific charge of full HE-NCM/C cells at different rates.* the comparison between the 5th and the 100th cycles to avoid the high irreversible charge loss of the first cycle coming from the activation of Li₂MnO₃ domains.

Galvanostatic curves of full-cells cycled at C/10 and 1 C rate are represented in the Figure 2.

In both cases we can see the passivation of the graphite around 3.1 V vs. Li⁺/Li at C/10 and at 3.4 V vs. Li⁺/Li at 1 C rate respectively. One can also notice the long potential plateau ascribable to the activation of Li₂MnO₃ domains linked to the release of oxygen.^{13,14} The most

interesting feature comes from the different polarisation of the cells between the rates. So far the results seems similar at C/10 rate, where the polarisation is the same between the 2nd and 50th cycle. However at 1 C rate another behavior can be observed with an increase of the polarisation between the 2nd and 50th cycle. This increase is most probably attributed to the surface layer building up which leads to an increase of the internal resistance during cycling. In order to validate our theory about the surface layer, we performed SEM and XPS post mortem analysis as drescribed in the next paragraph.

Figure 2. Galvanostatic curves of full HE-NCM/C cells of the 1st (black curve), 2nd (red curve), and 50th (blue curve) cycle for cells at 1 C and C/10 rate.

SEM analysis:

Post-mortem SEM images of HE-NCM electrodes cycled for 100 cycles at the slow C/10 rate are shown in Figure 3 top. There is almost no difference in the morphology for electrodes collected from half- and full-cells, and the electrolyte's decomposition seems to play a "minimal role". However, there are several small cracks on the surface of some HE-NCM particles (not present in the pristine electrode) which are not observed prior cycling. They likely

result from structural reorganization during cycling and/or from the oxygen release. Note that the particles are all covered with the Super P carbon and the binder, in addition to electrolyte decomposition products.

Figure 3. SEM images of HE-NCM electrodes cycled at top) C/10 rate, after 100 cycles; bottom) 1 C rate, after 300 cycles.

Figure 3 bottom shows the images from a similar analysis of electrodes cycled at the faster 1 C rate; at this rate, the electrodes, especially those that had been in the full-cells, are much more degraded in respect to their morphology.

Figure 4 top shows images of graphite electrodes cycled at the slow C/10 rate, and reveals significant differences between the electrodes from the half- and full-cells. For samples from full-cells, the graphite surface is completely covered by a polymer-like layer, which hides the graphite flakes, revealing that the electrolyte decomposition is more pronounced on the negative electrode. This can be explained by considering reports which indicate that transition

metals (which leach from the positive electrode) can be transported through the electrolyte.¹⁵ Once at the negative electrode, they are deposited on the graphite and/or react with the SEI and could catalyze the electrolyte decomposition, leading to the thicker SEI, as observed in our case^{16, 17}. However, the graphite flakes for electrodes cycled in the full-cell configuration are covered with small crystallized plate-like particles.

Figure 4. SEM images of graphite electrodes cycled at top) C/10 rate, after 100 cycles; bottom) 1 C rate, after 300 cycles.

The SEM images of graphite electrodes cycled at 1 C rate in LP30 electrolytes in half cell configuration appear similar to those from cells cycled at the C/10 rate in half-cell configuration. However, the difference between the electrodes cycled in full cell configuration but at two different rates is impressive. At C/10 we noticed a thick “polymer” covering all the graphite sheets, whereas the graphite sheets are still visible and slightly cover by a polymeric

layer at 1 C rate. This difference can be due to the different calendaring time between the 2 different tests.

By linking the SEM image analysis with the electrochemical results it becomes apparent that the surface layer that accumulates on the graphite electrodes in full-cells is different from the one observed in half-cells and most likely is linked the hampered electrochemical performances.

As expected, the surface of the HE-NCM electrodes seems to suffer less than the graphite by the impact of the electrolyte decomposition. Thus, as is consistent with the discussion in the literature¹⁸, the limitation of the full-cells seems to be in the graphite electrode, or at least the decomposition products observed on its surface.

XPS analysis:

Figure 4 presents the XPS core levels of C1s, O1s, Co2p, and Mn2p for HE-NCM electrodes cycled at rates of 1 C (250 cycles) and C/10 (100 cycles), and for an uncycled pristine electrode.

The C1s core level of the uncycled electrode displays a narrow main peak at 284.4 eV assigned to the C-C bonds of the Super P particles.¹⁹ Two other peaks are observed at 286.4 eV and 290.8 eV and result from CH₂ and CF₂ bonds in PVDF, respectively. Additional minor peaks are also present at 285.5 eV (hydrocarbons), 286.7 eV (ether C-O), 287.8 eV (carbonyl C=O), 288.9 eV (carboxyl O-C=O), and 290.1 eV (carbonate Li₂CO₃/CO₃).²⁰ The hydrocarbons and oxidized carbons likely result from the surface reaction of carbon particles with atmospheric oxygen and moisture. Meanwhile, the Li₂CO₃ present is most likely formed through an interaction between atmospheric CO₂ and the ion-mixed region in the Li(MnNiCo)O₂.²¹

The deconvolution of the O1s core level shows an intense peak at 529.6 eV corresponding to Li(MnNiCo)O₂. Additional components shifted to a higher binding energy (BE) are also

observed, namely at 531.5 eV (carbonate Li_2CO_3), 532.5 eV (carbonyl $\text{C}=\text{O}$), and 533.5 eV (ether $\text{C}-\text{O}$).

The $\text{Co}2\text{p}$ core level shows spin orbit peaks at 780.5 eV ($2\text{p}_{3/2}$) and 795.6 eV ($2\text{p}_{1/2}$). Given the peaks' binding energy positions and the absence of the satellite (S) at about 787 eV characteristic of octahedral Co^{2+} , the Co is likely in the trivalent state, as is expected for HE-NCM.¹⁹ The $\text{Mn}2\text{p}$ core level is similar, with two spin orbit peaks at 642.5 eV ($2\text{p}_{3/2}$) and 654.3 eV ($2\text{p}_{1/2}$). Likewise, given the absence of a satellite (S') peak expected at about 648 eV and characteristic of Mn^{2+} , we can conclude that Mn is likely in an oxidation state of 4+.¹⁵

After cycling at the C/10 and 1 C rate, the peak intensity in spectra from the HE-NCM particles in the $\text{O}1\text{s}$ core level decreases (Figure 5) while the intensity of the minor peaks originating from the surface layer increases. This confirms that surface layer formation leads to attenuation of the signal from the HE-NCM particles. Furthermore, greater noise of these (normalized to the C-C peak) peaks in the 1 C rate sample spectrum reveals that the SPI (Solid Permeable Interphase) is thicker at the 1 C rate than at the C/10 rate. However, note that there is a slight decrease in peak intensity for Super P in the 1 C rate spectrum and almost no increase in the C/10 case spectrum for the $\text{C}1\text{s}$ core level. No obvious change is observed for the $\text{Co}2\text{p}$ or $\text{Mn}2\text{p}$ spectra for the C/10 rate; however, at the 1 C rate, the $\text{Co}2\text{p}$ peaks are within the noise level while the $\text{Mn}2\text{p}$ peaks undergo a broadening at low and high binding energies. This broadening in $\text{Mn}2\text{p}$ peaks may result from the presence of Mn in lower oxidation states.^{16, 17}

Figure 5. C1s, O1s, Co2p, and Mn2p XPS core levels acquired on both pristine HE-NCM electrodes and HE-NCM electrodes after cycling at C/10 (100 cycles) and 1 C (300 cycles) rates in a full-cell configuration with LP30 electrolyte.

The XPS spectra of the graphite electrodes are presented in Figure 6. The C1s spectra confirm the SEM observation (Figure 3); for the C/10 rate the peak corresponding to graphite and Super P (284.5 eV) is not the most intense peak as expected but hidden by other contribution from the formation of a thick SEI layer. Indeed, additional components, associated with electrolyte decomposition and surface layer formation, are present at higher binding energies.

However, at the 1 C rate in full cell configuration, the graphite/Super P signal is more visible than at C/10, which is in agreement with the thinner polymer layer observed by SEM (Figure 4). According to us and to those observations, the difference in composition can come from the difference in calendar life of the electrodes. However we can also notice that the position of the peaks related to electrolyte decomposition is completely different leading us to conclude that the time in oxidation region during cycling changes the interfaces.

Unsurprisingly, transition metals, including Co and Mn, are present on the surface of the graphite electrode after cycling. At the C/10 rate, the presence of lower oxidation state Co^{2+} and Mn^{2+} is confirmed by satellite peaks at about 787 eV and 648 eV in the $\text{Co}2\text{p}$ and $\text{Mn}2\text{p}$ spectra, respectively. However, at the 1 C rate, the corresponding signal in the $\text{Co}2\text{p}$ spectrum is below the detection limit (maybe not observed because of the difference in calendar life between C/10 and 1 C rate).

The reason for the difference in the SEI thickness between the negative electrodes cycled at C/10 and 1 C is not fully understood. However, we can postulate some theories such as i) there is a difference in calendar life between the 2 electrodes cycled at C/10 and 1 C rate or ii) from the SEM images, this effect seems to be directly related to the fading of electrochemical activities of the cell at the C/10 rate.

Figure 6. $\text{C}1\text{s}$, $\text{Co}2\text{p}$, and $\text{Mn}2\text{p}$ XPS core levels acquired on graphite electrodes after cycling at C/10 (100 cycles) and 1 C (300 cycles) rates in a full-cell configuration with LP30 electrolyte.

In summary, the graphite negative electrode is not the only factor responsible for the low cycling performance in full-cells; rather, the dissolution of transition metals from the positive electrode and their migration to the negative electrode indicates that it is more the strong

interaction between the positive and the negative electrodes influencing the course of the cycling, as found by K. Amine et al with lithium manganese oxide versus graphite.²²

Conclusions

We have demonstrated good cyclability of full-cells containing HE-NCM and graphite active materials within the cut-off voltage limits of 1.0 V-4.8 V. Different cycling rates were used, ranging from C/10 to 1 C, and a specific charge higher than 150 mAh/g (in respect to HE-NCM) was observed for full-cells even after 250 cycles. Furthermore, the cells were able to deliver a specific charge of more than 100 mAh/g even after 600 cycles for the C/2 rate. *Post-mortem* SEM analysis showed that, in full-cells the most pronounced changes occurred on the surface of the graphite, preventing thus proper cycling. Meanwhile, the *post-mortem* XPS analysis showed that transition metals are able to be transferred through the electrolyte from the positive to the negative electrode.

269 Acknowledgments

270 The authors thank the BASF Network Electrochemistry and Batteries for the financial support
271 and scientific discussions.

273 References

- 274 1. Yabuuchi, N.; Ohzuku, T., Novel lithium insertion material of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$
275 for advanced lithium-ion batteries. *J. Power Sources* **2003**, 119-121, 171-174.
- 276 2. Robert, R.; Villevieille, C.; Novak, P., Enhancement of the high potential specific
277 charge in layered electrode materials for lithium-ion batteries. *J. Mater. Chem. A* **2014**, 2,
278 8589.
- 279 3. Kim, J. M.; Kumagai, N.; Kadoma, Y.; Yashiro, H., Synthesis and electrochemical
280 properties of lithium non-stoichiometric $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_{2+\delta}$ prepared by a
281 spray drying method. *J. Power Sources* **2007**, 174, (2), 473-479.
- 282 4. Tran, N.; Croguennec, L.; Menetrier, M.; Weill, F.; Biensan, P.; Jordy, C.; Delmas,
283 C., Mechanisms associated with the "Plateau" observed at high voltage for the overlithiated
284 $\text{Li}_{1.12}(\text{Ni}_{0.425}\text{Mn}_{0.425}\text{Co}_{0.15})(0.88)\text{O}_{-2}$ system. *Chemistry of Materials* **2008**, 20, (15),
285 4815-4825.
- 286 5. Park, J.; Seo, J. H.; Plett, G.; Lu, W.; Sastry, A. M., Numerical Simulation of the
287 Effect of the Dissolution of LiMn_2O_4 Particles on Li-Ion Battery Performance. *Electrochem.*
288 *Solid State Lett.* **2011**, 14, (2), A14-A18.
- 289 6. Deng, Z. Q.; Manthiram, A., Influence of Cationic Substitutions on the Oxygen Loss
290 and Reversible Capacity of Lithium-Rich Layered Oxide Cathodes. *J. Phys. Chem. C* **2011**,
291 115, (14), 7097-7103.
- 292 7. Lee, H.; Choi, S.; Choi, S.; Kim, H. J.; Choi, Y.; Yoon, S.; Cho, J. J., SEI layer-
293 forming additives for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{graphite}$ 5 V Li-ion batteries. *Electrochem. Commun.*
294 **2007**, 9, (4), 801-806.
- 295 8. Liu, M. H.; Dai, F.; Ma, Z. R.; Ruthkosky, M.; Yang, L., Improved electrolyte and its
296 application in $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ -Graphite full cells. *J. Power Sources* **2014**, 268, 37-44.
- 297 9. Villevieille, C.; Lanz, P.; Bunzli, C.; Novak, P., Bulk and surface analyses of ageing
298 of a 5V-NCM positive electrode material for lithium-ion batteries. *J. Mater. Chem. A* **2014**, 2,
299 (18), 6488-6493.
- 300 10. Villevieille, C.; Lanz, P.; Buenzli, C.; Novak, P., Bulk and surface analyses of ageing
301 of a 5V-NCM positive electrode material for lithium-ion batteries. *J. Mater. Chem. A* **2014**, 2,
302 (18), 6488-6493.
- 303 11. Villevieille, C.; Gomez, J. L.; Hess, M.; Novak, P., Reducing mass transfer effects on
304 the kinetics of 5V HE-NCM electrode materials for Li-ion batteries. *Journal of*
305 *Electrochemical Society* **2014**, 161 A871.
- 306 12. Lanz, P.; Villevieille, C.; Novák, P., Ex situ and in situ Raman microscopic
307 investigation of the differences between stoichiometric LiMO_2 and high-energy
308 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M} = \text{Ni, Co, Mn}$). *Electrochim. Acta* **2014**, 130, (0), 206-212.
- 309 13. Castel, E.; Berg, E. J.; El Kazzi, M.; Novak, P.; Villevieille, C., Differential
310 Electrochemical Mass Spectrometry Study of the Interface of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M} = \text{Ni, Co, and Mn}$)
311 Material as a Positive Electrode in Li-Ion Batteries.
312 *Chemistry of Materials* **2014**, 26, (17), 5051-5057.

14. Massarotti, V.; Capsoni, D.; Bini, M.; Azzoni, C. B.; Paleari, A., Stoichiometry of Li₂MnO₃ and LiMn₂O₄ coexisting phases: XRD and EPR characterization. *J. Solid State Chem.* **1997**, 128, (1), 80-86.
15. Vetter, J.; Novák, P.; Wagner, M. R.; Veit, C.; Moeller, K. C.; Besenhard, J. O.; Winter, M.; Wohlfahrt-Mehrens, M.; Vogler, C.; Hammouche, A., Ageing mechanisms in lithium-ion batteries. *J. Power Sources* **2005**, 147, (1-2), 269-281.
16. Pieczonka, N. P. W.; Liu, Z. Y.; Lu, P.; Olson, K. L.; Moote, J.; Powell, B. R.; Kim, J. H., Understanding Transition-Metal Dissolution Behavior in LiNi_{0.5}Mn_{1.5}O₄ High-Voltage Spinel for Lithium Ion Batteries. *J. Phys. Chem. C* **2013**, 117, (31), 15947-15957.
17. Gallus, D. R.; Schmitz, R.; Wagner, R.; Hoffmann, B.; Nowak, S.; Cekic-Laskovic, I.; Schmitz, R. W.; Winter, M., The influence of different conducting salts on the metal dissolution and capacity fading of NCM cathode material. *Electrochim. Acta* **2014**, 134, 393-398.
18. Li, Y.; Bettge, M.; Polzin, B.; Zhu, Y.; Balasubramanian, M.; Abraham, D. P., Understanding Long-Term Cycling Performance of Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O₂-Graphite Lithium-Ion Cells. *J. Electrochem. Soc.* **2013**, 160, (5), A3006-A3019.
19. Kim, J. G.; Pugmire, D. L.; Battaglia, D.; Langell, M., Analysis of the NiCo₂O₄ spinel surface with Auger and X-ray photoelectron spectroscopy. *Applied Surface Science* **2000**, 165, 70.
20. Verma, P.; Maire, P.; Novak, P., A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries. *Electrochim. Acta* **2010**, 55, (22), 6332-6341.
21. Andersson, A. M.; Abraham, D. P.; Haasch, R.; MacLaren, S.; Liu, J.; Amine, K., Surface characterization of electrodes from high power lithium-ion batteries. *J. Electrochem. Soc.* **2002**, 149, (10), A1358-A1369.
22. Zhan, C.; Lu, J.; Kropf, A. J.; Wu, T. P.; Jansen, A. N.; Sun, Y. K.; Qiu, X. P.; Amine, K., Mn(II) deposition on anodes and its effects on capacity fade in spinel lithium manganate-carbon systems. *Nat. Commun.* **2013**, 4, 8.