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# Highly densified NCM-cathodes for high energy Li-ion batteries: Microstructural evolution during densification and its influence on the performance of the electrodes

Denny Schmidt[a,*], Marc Kamlah[b], Volker Knoblauch[c]

[a] Robert Bosch Battery Systems GmbH, Kruppstraße 20, 70469, Stuttgart, Germany
[b] Karlsruhe Institute of Technology, Institute of Applied Material (IAM), Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany
[c] Aalen University, Materials Research Institute (IMFAA), Beethovenstraße 1, 73430, Aalen, Germany,

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ABSTRACT

For positive electrodes in Lithium ion batteries $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) is widely used as an active material. The performance of the electrodes in different applications is mainly influenced through the electrode manufacturing process. This work aims to contribute to a better understanding of the relation between microstructure development caused by the densification of the electrodes and its influence on electrochemical behaviour as well as ageing. Therefore, NCM-based cathodes were compacted in several interstages down to a porosity of 18%. By detailed microscopic analyses and Hg porosimetry we provide important insights concerning the electrodes microstructure, its evolution during densification and the correlation to the electrochemical performance. In doing so it will become obvious that major microstructural changes take place when electrodes are compacted to porosities below 22–25% which goes along with a significant decline of the capacity and energy density at current rates of 2C and more. However, at current rates below 1C the highest energy density is observed for cathodes with even lower porosities. Additionally, the microscopic analyses provide important information about how this problem can be tackled.

## 1. Introduction

Lithium ion batteries (LIB) are indisputably omnipresent in consumer electronics since their introduction into the market at the beginning of the 1990s. During the last decades, the field of application is continuously expanding in mobile and stationary energy storage. The requirement profile is demanding and primarily aims on higher energy and power densities, better lifetime, safety and lower costs [1,2]. Various kinds of active materials are discussed with increasing intensity in literature regarding their influence on electrochemical capability. A special focus is on varying the active material morphology, particle size, surface modification as well as composition of the active mass. In this respect, we refer to the review articles [3–8].

Whereas the equilibrium cell voltage is solely defined by the active materials the non-equilibrium electrochemical performance is essentially determined by the microstructure of the electrodes – which is adjusted during electrode manufacturing, in detail by slurry fabrication, coating, drying and calendering [9–11]. Calendering as the last step of electrode manufacturing decreases electrodes porosity and thickness. Thus, it strongly affects volumetric properties, such as capacity density and, accordingly, energy as well as power density [12–15]. Lithium ion battery electrodes are composed of different components and phases (active material, conductive additives, binder and pores filled with electrolyte) to offer, roughly summarized, good electrical and ionic conductivity equally. Ion transport within and between the electrodes during operation requires a pore network [16]. On the other hand, compaction of the electrode increases the electrical conductivity within the electrodes and between electrode and current collector, respectively [17,18]. As a consequence, electric and ionic conductivity change inversely to each other under increasing electrode densification [19]. While electric conductivity increases by moderate compaction, because of an improved formation of electric conductive pathways, ionic conductivity decreases due to progressively sealed percolation paths especially at the transition from moderate to high compaction (porosity ≤ 25%). Generally, the (de-)lithiation process within the highly densified active material is inhibited by

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* Corresponding author.
*E-mail addresses:* denny.schmidt@de.bosch.com (D. Schmidt), marc.kamlah@kit.edu (M. Kamlah), volker.knoblauch@hs-aalen.de (V. Knoblauch).

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lowered wetting of the electrode surface with electrolyte and reduced ionic conductivity [20].

In order to increase the energy density of battery cells and thus the driving range of electrical cars, cell manufacturers strive – among other approaches – to increase the density of the electrodes by highly compacting them. However, it is necessary to find the right balance between high compaction rates to ensure a high (theoretical) energy density and a high ionic conductivity, respectively a fully developed pore network, which is indispensable when the cells are operated with higher current rates (C-rates). To do so, a deep understanding of microstructural evolution during densification and its correlation with the electrochemical performance is needed. Even though continuative results are published on the compaction of electrodes and their corresponding electrochemical performance [8,14–16,21–24], there are only a very few papers that present results for highly densified cathodes [25,26]. Moreover, microstructural analyses are often restricted to the overall porosity derived from the electrodes density limiting the interpretation of the electrochemical data.

## 2. Experimental

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM111, hereafter named NCM) cathode active material and carbon-based conductive additives were mixed in an N-Methyl-2-pyrrolidone (NMP)-solved polyvinylidene fluoride (PVdF)-binder by mechanical dissolver mixing up to 2000 rpm for approx. 4 h. Subsequently, an aluminium current collector (foil with a thickness of 15 $\mu$m) was coated one-sided with slurry using the doctor blade method (slot size: 275 $\mu$m). The electrodes were finally dried in a fume hood at room temperature. Cathode active mass was composed of 92 wt% NCM active material, 4 wt% binder and 4 wt% additives, respectively. To prepare the electrodes for compaction and microstructural as well as electrochemical investigations circular samples with a diameter of 10 mm were cut by a precision die cutter (Nogami). To be able to uniformly and highly densify the electrodes in a reproducible way [26], the samples were compacted by uniaxial compressive loading in a load frame. To do so, we used a surface polished and ball bearing mounted pressing tool (diameter: 20 mm each side) in a universal testing machine (RSA 100; Schenk). Different uniaxial compaction loads of 100, 200, 300, 400, 500, 750 and 1000 MPa measured by an integrated load cell were applied in quasi-static mode. The overall resulting porosity $\varepsilon$ was calculated by the ratio of the bulk density $\rho_B$ of the active mass and the skeleton density $\rho_S$. The skeleton density was determined by analysing the individual components with a He-pycnometer (AccuPyc 1330; Micromeritics), while the bulk density was calculated out of the given active mass weight and the sample volume including porosity, determined by sample diameter and the film thickness at the respective compaction load.

Microstructural characterisation was carried out by a scanning electron microscope (SEM Gemini 1525; Zeiss) on the surface as well as in cross section view. For this purpose, the samples were vertically embedded in an epoxy-resin (Epofix; Struers) and the surface was grinded and polished with 9, 3, 1 and 0.25 $\mu$m-diamond suspension (Tegramin 30; Struers). Beside porosity, the phase fraction of NCM – which represents the amount of NCM particles in the active mass – was determined as an additional parameter to describe the densification. This was done by means of Quantitative Microstructural Analysis as described in Ref. [27] using light microscopic images (AxioPlan2; Zeiss). Additionally, focus ion beam (FIB) preparation and SEM-analyses (Ga-FIB/SEM crossbeam 540; Zeiss) were carried out starting from a platinic surface in order to gain a better understanding of the microstructural evolution especially for high compaction rates. Porosity, pore sizes and pore size distribution were determined by Hg porosimetry (Pascal 140–440; Porotec) with a total scan pressure up to 400 MPa. [28] provides an overview about the prospects of mercury intrusion to characterise the electrode microstructure with focus on pores and pore network properties. The tortuosity $\tau$, calculated according to Ref. [29], describes the degree of curling of transport paths inside porous materials and characterizes indirectly the physical transport processes of Lithium ions within the pore network of the active mass.

To evaluate the electrochemical performance of the differently compacted cathodes separately and to largely eliminate side effects from anodes, half-cell tests were performed firstly. Before assembling the cells in an Argon filled glovebox (Sylatech), the electrodes were dried at 80°C for at least 8 h in a vacuum oven (Heraeus). The one-side coated cathodes were assembled in 2-electrode-Swagelok-configuration vs. Lithium (diameter 11 mm, thickness: 0.75 mm; AlfaAesar). A glass fibre separator (GF/C; Whatman, diameter: 12 mm; thickness: 0.26 mm) was used and the electrolyte was 1 mol $LiPF_6$ at 3:7 EC/EMC with additives (300 $\mu$l per test cell). The test cells were analysed with a potentiostat (CTS-Lab; BaSyTec) in a climate chamber (T-40/200/Li; CTS) at 20 °C. The charging mode consisted of a galvanostatic (constant current, CC) part up to 4.3 V and a potentiostatic (constant voltage, CV) part [30]. The discharge mode was galvanostatic down to 2.6 V. The current rate (C-rate) in the galvanostatic regime was the same for the charge and discharge step. The electrochemical performance (e.g. specific capacity and capacity density) of the cathodes was determined by the cycling protocol listed in Table 1. The loading level (defined as the weight of the active material per unit area) and the capacity per unit area of the different compacted cathodes was constant. Reproducibility was ensured by testing of at least five test cells with equally defined parameters. The maximum standard deviation was in the range of 2.5% in all cases and hence, is not plotted in the diagrams in order not to overload them. Weight related parameters (gravimetric) were based on the NCM active material weight, exclusive binder, additives and current collector foil. On the other hand, the sample volume to calculate the volumetric parameters were determined by the active mass volume which includes the volume of the active material, binder, additives and pores, however excluding the collector foil. To calculate the energy and power densities, we used the different discharge capacities and illustrated the results according to Ragone (Energy [Wh] vs. Power [W]) [32].

Full-cell performance and accelerated ageing behaviour of the differently compacted cathodes were determined using graphite anodes with a copper foil as current collector (diameter: 11 mm to ensure an overlap of the anode versus the cathode) in 3-electrode-Swagelok-configuration with Lithium as reference electrode. The anode parameters were kept constant with a loading level of 7.86 $mg/cm^2$ (respectively 2.87 $mAh/cm^2$ based on the theoretical capacity of graphite of 372 mAh/g [2]; the ratio of the negative and positive electrode (n/p) was 1.16) and a porosity of 30%. The cycle protocol for the full-cell tests was composed of the following steps: 2 × C/5, 50 × 2C and finally 2 x C/5 between 4.2 and 2.5 V. With this kind of accelerated ageing tests, we intended to get first insights in the ageing behaviour of full-cells and the effect of densification, respectively ionic and electronic transport. The number of 50 cycles at 2C was chosen as a compromise between a significant loading of the cells and an acceptable duration of the experiments.

**Table 1**
Cycle protocol for half-cell configuration: NCM vs. Lithium ($Li/Li^+$).

| Cycle step | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| C-rate | C/20 | C/10 | C/5 | C/2 | 1C | 2C | 3C | 5C | C/5 |
| Cut-off current in CV step | C/30 | C/20 | C/20 | C/10 | C/5 | C/5 | C/5 | C/5 | C/20 |
| Cycle counts | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |