



Characterization of the calendaring process for compaction of electrodes for lithium-ion batteries



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ABSTRACT

Calendering is the common compaction process for lithium-ion battery electrodes and has a substantial impact on the pore structure and therefore the electrochemical performance of Lithium-ion battery cells. For a targeted determination of the performance-optimized pore structure, it is of decisive importance to be able to comprehensively control the compaction process. Thus, during continuous calendaring of graphite anodes and lithium nickel cobalt manganese oxide (NCM) cathodes the applied line load is tracked and varied at different speeds to compact the electrode to several coating densities. The generated pore structures are measured via mercury intrusion, resulting in quite similar porosities, while the densities of graphite and NCM diverge greatly. The porosities, measured via mercury intrusion, are compared to geometrical determined data, identifying compaction resistant closed pores in the NCM. On the basis of the measured porosity reduction the compaction behavior of the line load was found to be describable by an exponential model equation. The model parameters quantify the different compaction resistances of the cathodes and anodes in converging to a maximal density, respectively minimal porosity. This substantial difference could be traced to the closer packing of the spherical and harder NCM particles. The calendaring speed showed only an insignificant impact up to speeds of 5 m/min.

1. Introduction

Possibly, the most important characteristic of an energy storage system is its energy density. The volumetric energy density is crucial, especially for portable systems or electromobility purposes with a limited space. In the process chain of lithium-ion battery electrode manufacturing, the coating porosity, and with that the energy content per volume is most decisively determined by the compaction step. In research, mainly uniaxial hydraulic presses are used, whereas roll presses or calenders of technical scale are rarely utilized. Nevertheless, the compaction between two rolls working in opposite directions as depicted in Fig. 1 is the established continuous method for industrial purposes. The electrode, a current collector foil (copper for anodes or aluminum for cathodes) coated with the particulate coating on both sides, gets pulled into the gap. For process control either the gap size is set significantly smaller than the electrode thickness or the rolling force is adjusted ensuring the desired compaction of the electrodes coating. Leaving the gap the coating undergoes an elastic relaxation. Details regarding the used machine and its specific mechanical realization of the principle are explained in Chapter 2.2.

Until today less attention is paid to the necessary applied

mechanical forces respectively line loads, whereas electrochemical properties of differently compacted electrodes are often attributed. The huge influence on the electrochemical performance, compared to other process steps, is due to drastic changes in the pore structure of the particulate coating of the electrodes.

The changes achieved by calendaring are very different for anodes and cathodes, mainly because of the diverging material properties. Shim and Striebel (2003) demonstrated, that moderate compaction can decrease the irreversible capacity loss and the ohmic contact resistance and as Striebel et al. (2004) augmented also the electrochemical impedance. On the other hand Wilka (2013) showed, that the calendaring of the anode leads to an increasing diffusive resistance due to the porosity loss. Regarding mechanical properties, Haselrieder et al. (2013) demonstrated, that a moderate compaction of anodes decreases the plasticity of the coating and enables better reversible intercalation processes enabling a higher cycling stability. However, Wang et al. (2004) warned of too high loads causing particle fracture. Concerning the compaction process itself, Manev et al. (1995) already pointed out, that longer hold times during uniaxial compaction lead to a significant smaller porosity indicating that the velocity of the compaction process in hydraulic pressing matters a lot. Using uniaxial hot pressing for

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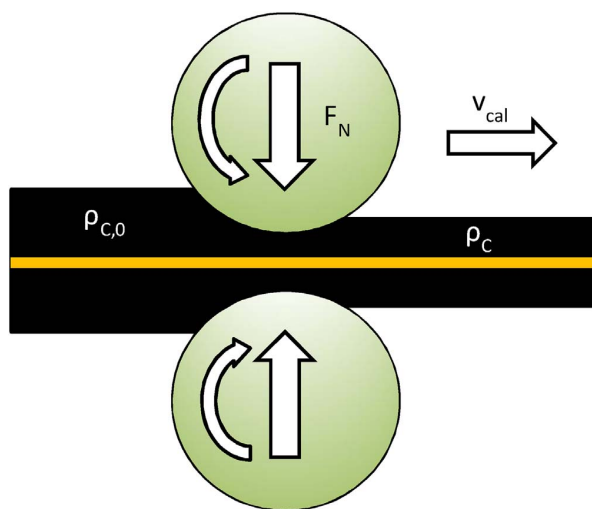


Fig. 1. Sketch of the calendaring process including the product properties initial coating density $\rho_{C,0}$ and processed coating density ρ_C as well as the process parameters rolling force F_N and circumferential speed v_{cal} . The latter one represents also the calendaring velocity.

densification of electrodes, Antartis et al. (2015) investigated the influence of the applied pressure but did not correlated it with the density or porosity of the anodes via an model equation. They found a narrow optimum in electrochemical and mechanical characteristics at 45% porosity.

As the specific electric conductivity of cathode active materials is much lower, its embedment in the electrode's carbon black matrix is much more important than for anode materials. Ott et al. (2013) transferred a fast and flexible resistor-network model for the micro-structural influence on the effective conductivity of lithium-ion battery electrodes, which was developed by Völker and McMeeking (2012) for the in solid oxide fuel cell electrodes. They show a positive influence of solid volume fraction and size ratio of ionic conductive and electronic conductive particles and especially for lithium-ion battery electrodes of the volume expansion of the active particles during lithium-ion intercalation and uniaxial compaction on the effective conductivity. The embedment of particles in the conductive network is also highly affected by the formulation as addressed by Liu et al. (2012), influences the initial coating structure before compaction and therefore also the compaction behavior of the coating. Subsequently, the compaction modifies and enhances this embedment, which results usually in a much higher conductivity of the coating. Thus, simultaneous increases in diffusive resistance are less restricting, which is found for LCO by Gnanaraj et al. (2001) and for LFP by Bommel and Divigalpitiya (2012). In addition, for NCM a desirable increase of the adhesion strength is reported by Marks et al. (2011), whereas Li et al. (2012) pointed out, that the tortuosity inside the particulate coating increases, and, thus, wetting problems are to be expected. Another major negative effect is the reduction of the available capacity at high C-rates due to low ionic conductivity and is reported by Lu et al. (2011) for LFP at 10C, by Chu et al. (2012) for LCO-electrodes at 3C and by Rauscher (2014) for LMS/NCA hybrid electrodes of high mass loadings at 7.5C. Schilcher et al. (2016) additionally demonstrated the high importance of the optimal density for mechanically sensible materials like LMO regarding particle fracture, which leads to an aging acceleration of the manufactured cells.

However, there is always a rather narrow range in density, respectively porosity, which results in optimal physical and mechanical characteristics and enhanced electrochemical performance of electrodes for lithium-ion batteries. Thus, the demand of knowledge-based electrode densification in relevant compaction machines, i.e., calenders, is very high and it is decisive to be able to predict the needed

Table 1

Characteristics of the provided NCM cathodes and graphite anodes (* material specifications by datasheet of provider).

	NCM cathode	graphite anode
active material		
- particle shape	spheres ^a	flakes ^a
- particle size	$x_{50,3} = 12 \mu\text{m}^a$	$x_{avg} = 20,9 \mu\text{m}^a$
mass fractions in the coating [wt%]		
- active material	86	85
- conductive carbon	4	5
- graphite additives	4	0
- binder	6	10
volume fractions in the uncalendered coating [vol%]		
- active material	31 ^a	32 ^a
- conductive carbon	4 ^a	3 ^a
- graphite additives	3 ^a	0 ^a
- binder	6 ^a	5 ^a
- porosity	57 ^a	61 ^a
measured electrode data:		
current collector material	Al	Cu
current collector thickness [μm]	20.0 ± 0.6	17.3 ± 0.7
mass loading [g/m^2] (sums of both coated sides)	451.0 ± 14.0	196.8 ± 3.2
coating thickness [μm] (sums of both coated sides)	267.1 ± 3.5	247.2 ± 4.0
geometrical porosity [%] (uncalendered) ^b	57.0 ± 1.2	60.8 ± 0.5

^a The numbers do not add up to 100 due to rounding errors.

^b Definition in Chapter 2.3.

compaction load to achieve the desired pore structure. The present contribution aims to derive a predictive equation for the determination of the applied line load for a demanded density increase and porosity decrease of lithium-ion battery electrodes by calendaring.

2. Material and methods

2.1. Electrode composition

The compositions and measured characteristics of the electrodes used in this study are displayed in Table 1. Current collectors were coated on both sides. Please note, that due to the formulation changes no direct comparison between anodes and cathodes is possible. However, the aim is to show the applicability of the new model to two very different electrodes.

2.2. Calendaring

The electrodes were compacted by a pilot scale two roll compactor in a pilot scale continuous process (Saueressig GmbH Co KG, Germany). The two identical rolls measure 450 mm in diameter and 470 mm in width. The maximal applicable line load is 1500 N/mm. The appropriated electrodes have coating widths of 200 mm and were calendered at ambient temperature and with two different roller speeds. The different line loads were applied by varying the gap size between the rolls.

The calender operates with two pairs of cylinders: the main cylinders (M) and the roll bending cylinders (RB). The latter one ensures minimization of the crowning effect. Both pairs build a force balance, when the gap is set. As the RB-cylinders press the rolls towards each other, the main cylinders press them apart. An electrode passing the gap causes a load relief on the M-cylinders. This difference is regarded as the rolling force applied F_N on the electrode.

Considering the rolling force F_N over the time of one electrode passage through the gap, it could be identified, that the force rises abruptly to a plateau with fluctuations and decreases as the electrodes leaves the gap (see Fig. 2). To avoid consideration of outliers, a BoxPlot method referring to Tukey (1977) is used. The mean value for the rolling force is determined out of the Box data including the whiskers.

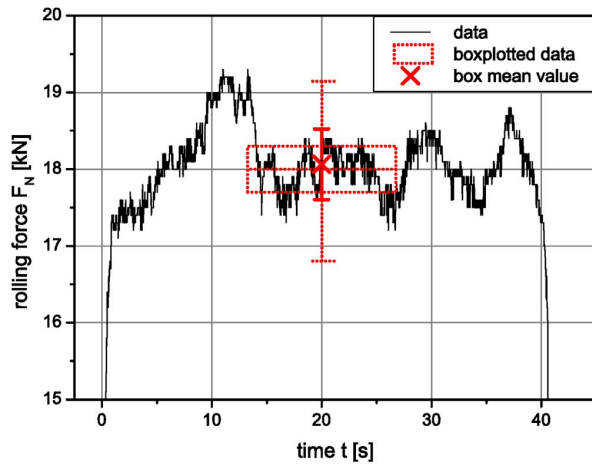


Fig. 2. Determination of the mean rolling force F_N by the Boxplot method. Example: graphite anode calendered to $\rho_C = 1.28 \text{ g/cm}^3$ at $v_{\text{cal}} = 5 \text{ m/min}$.

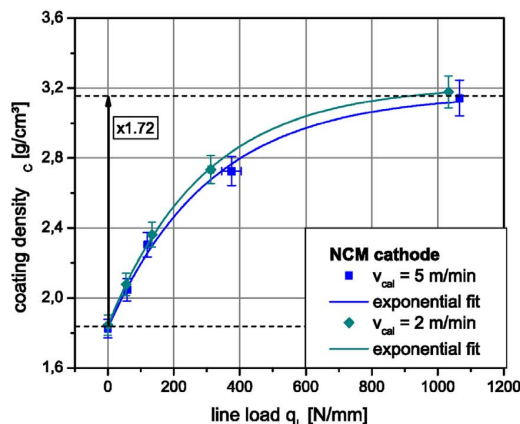
All measurements were done twice. The applied line load q_L is calculated from the rolling force F_N and the coating width w_C of the electrode: $q_L = F_N/w_C$.

2.3. Electrode characterization

The thicknesses of the electrodes h_E and current collector foils h_C were measured by a tactile dial gauge (ID-C, Mitutoyo, Japan) with a resolution of $1 \mu\text{m}$, the mass loadings m_E and m_S by weighing. Basis for the determined values are measurement patterns with single measurements covering a representative coating area of 600 cm^2 to control the homogenous coating and compaction. Assuming the incompressibility of the current collector, the coating density ρ_C , can be calculated by Eq. (1) for all calendered electrodes. The assumption is not fully justified as it is known that single particles penetrate the current collector to a depth of 1 or 2 micrometers due to very high compaction, shown by Tran et al. (2012). Nevertheless, the resulting error in measuring the thickness of a compound ($h_E > 125 \mu\text{m}$ at its highest compaction rate) is smaller than the possible deviations in thickness measurement.

$$\rho_C = \frac{m_E - m_C}{h_E - h_C} \quad (1)$$

m_E : mass loading of the electrode, m_C : mass loading of the current collector, h_E : thickness of the electrode, h_C : thickness of the current collector



The physical coating porosity $\varepsilon_{C,ph}$ was calculated from the coating density ρ_C and the mean physical density of the components ρ_{ph} , i.e. the material mixture, measured by gas pycnometry:

$$\varepsilon_{C,ph} = 1 - \frac{\rho_C}{\rho_{ph}} \quad (2)$$

The pore structure of the electrodes is determined by mercury intrusion (Hg porosimetry) using a PoreMaster 60 (Quantachrome Instruments, USA) and following the method of Froboese et al. (accepted). After evacuating the porous electrode inside the measuring cell, the non-wetting mercury (angle of contact $\theta_{Hg} = 140^\circ$, surface tension $\sigma_{Hg} = 0.48 \text{ N/m}$, following the convention of Zheng et al. (2010)) is pressed into the pores. As the system pressure gets increased, the diameter of the pores, which are filled by mercury, decreases following Equation of Washburn (1921). The applied pressure range for the gathered results is 1.45–206.3 MPa. All porosity measurements were carried out two times to increase measurement accuracy.

The results from mercury porosimetry measurements were used to determine the porosity of the coating in a second way. The hereby calculated coating porosity $\varepsilon_{C,Hg}$ is derived from the volumes of the intruded mercury $V_{Hg,i}$, the electrode sample V_{Sa} , and the substrate V_{Sub} , as shown in Eq. (3).

$$\varepsilon_{C,Hg} = \frac{V_{Hg,i}}{V_{Sa} - V_{Sub}} \quad (3)$$

3. Results and discussion

3.1. Characterization of the calendering compaction process

3.1.1. Density-based considerations

The compaction through calendering increases the coating density of the electrodes. The measured densities of the coating were plotted against the applied line load in Fig. 3. Results for graphite anodes and NCM cathodes are depicted. It was intended to reduce the coating thickness of both, the anode and the cathode, by the same value of about 40%, resulting in $40.0 \pm 0.5\%$ for the anodes and an achievable maximum of $38.9 \pm 0.2\%$ for the cathodes, what is equivalent to density increases by $75.4 \pm 1.5\%$ and $72.2 \pm 0.1\%$, respectively, as displayed in Fig. 3.

Attention should be paid to the different density scales: the NCM cathodes have a much higher initial density due to the higher physical density of the NCM particles (4.65 g/cm^3) compared to the graphite particles (2.26 g/cm^3).

In both cases there is only a very small, statistically not significant influence of the two different circumferential speeds, whereas smaller

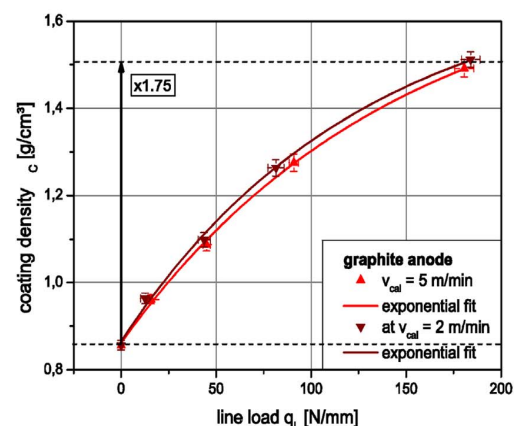


Fig. 3. Increase of the coating density of NCM cathodes (left) and graphite anodes (right) by calendering at different velocities and line loads. For the velocity comparison, the density increases are displayed.

Table 2

Approximation parameters for the different circumferential speed and electrodes.

	NCM cathode		graphite anode	
circumferential speed v_{cal} [m/min]	2	5	2	5
initial coating density $\rho_{c,0}$ [g/cm ³]	1.84 ± 0.02	1.83 ± 0.08	0.87 ± 0.09	0.86 ± 0.08
maximal coating density $\rho_{c,max}$ [g/cm ³]	3.21 ± 0.02	3.16 ± 0.08	1.71 ± 0.1	1.74 ± 0.09
compaction resistance γ_c [N/mm]	292 ± 9	309 ± 45	126 ± 26	144 ± 24

circumferential speeds tend to result in slightly higher densities. Therefore, some of the following investigations were carried out only at one velocity (5 m/min). The relation between the applied line load q_L and the measured density ρ_c can be described by an exponential approximation with the following parameters: initial coating density $\rho_{c,0}$, and as fitting parameters the maximal coating density $\rho_{c,max}$ and γ_c , which is named compaction resistance in the following (see Eq. (4)).

$$\rho_c = \rho_{c,max} - (\rho_{c,max} - \rho_{c,0}) \exp\left(-\frac{q_L}{\gamma_c}\right) \quad (4)$$

The exponential relation reminds of the compaction equation of Heckel (1961), which is used as the basis in several models describing the compressibility of powders, especially in the pharmaceutical application, discussed in detail by Li et al. (2012). The Heckel equation assumes a similarity to a first-order chemical reaction, substituting the time by the pressure and the concentration by the porosity/density. The resemblance to Eq. (4) shows, that this assumption is also accurate for the compaction of electrode coatings.

Table 2 shows the parameter values of the approximations for anodes and cathodes. $\rho_{c,0}$ describes the starting point of the compaction and $\rho_{c,max}$ the end point, according to the proposed approximation. The mean physical density of the material mixture at a theoretical porosity of 0% is 2.2 g/cm³ for the anode and 4.3 g/cm³ for the cathode, based on material density determination by gas pycnometry. Thus, the compaction windows of the anode and cathode have very different scales. For the cathode Eq. (4) predicts a maximal density of about 3.2 g/cm³, while for the anode the model yields an extrapolated maximal density of above 1.7 g/cm³. The latter one is significantly higher than the experimentally achieved density with line loads up to 200 N/mm. γ_c describes the shape of the curve: the lower the parameter γ_c , the earlier the coating density ρ_c converges to the maximum. Thus, the parameter γ_c can be considered as the compaction resistance of the electrode coating. The values for γ_c of the different electrode compactions are presented in Fig. 4. The standard errors result from the error propagation of the approximation. The error weighting method is

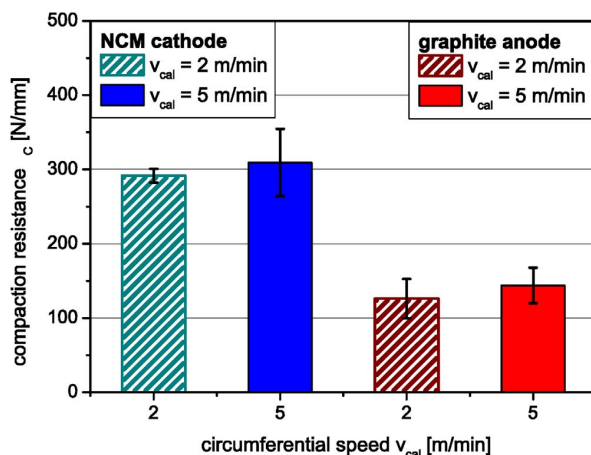


Fig. 4. The compaction resistance γ_c of different electrodes at different circumferential speeds.

instrumental, which means that the data is weighted by a reciprocal of the belonging standard errors. Again, there is only a statistically not significant dependence on the calendaring circumferential speed: the compaction resistance is slightly higher for 5 than for 2 m/min. However, the dependency on the material is distinct. The parameter γ_c for the NCM cathodes is almost twice as high as for the graphite anodes, i.e., the cathodes appear more resistive to compaction. Thus, for the cathodes it is necessary to apply a higher line load for a comparable compaction than for the anodes. The main solid amount of an electrode is the active material, here: NCM or graphite. It seems reasonable to suppose that their properties have a major influence on the compaction behavior of the electrode. The NCM particles are much harder than the graphite particles, and, hence higher forces have to be exerted to effectuate deformation in means of particle–particle rearrangements associated with particle friction, what is assumed but not clearly reduced to be the main reason for the differences.

Further major impact result from the different bulk material properties, affected by the composition (additive type and amount) in the coating, as well as particle's morphology and size distribution of active materials. As these parameters differ quite significantly for the exemplary used electrodes, the resulting initial pore structure and its influence on the compaction behavior, will be discussed in the following.

3.1.2. Determination of the pore structure

For a better comparability of electrodes with very different densities, it is of high interest to investigate the porosity. To compare the compactibility at different circumferential speeds in the previous chapter, the anode coating was compacted at both velocities to the same density range. In comparison of the porosities of both compacted anodes and cathodes, is to notice, that the achieved minimum of the anode porosity was significantly higher and the anode density is significantly lower than the extrapolated maximal density. This potential for higher compaction was used to compact the anode at 5 m/min additionally to the practically achievable density maximum of about 1.77 g/cm³, which corresponds the extrapolated maximal density (Table 2) within the limits of accuracy of the measurements.

Two methods to determine the porosity of the electrode coatings were used and compared. As shown by the mercury porosimetry measurements in Fig. 5, the pores of the coating appear between 8 nm and 10 μ m. Thus, this range was used for the porosity calculations. The porosimetry gains further information about the pore structure. The cathode (top left in Fig. 5) features a bimodal pore diameter distribution with one peak at about 0.1 μ m, which can be attributed to the pores between the carbon conductive particles, and another peak at about 1 μ m, which are attributed by Bockholt et al. (2016) to the pores among the NCM particles. The smaller and more spherical NCM particles generate a closer packing in comparison to the larger graphite flakes of the anode (down left in Fig. 5). Consequently, the peak, which represents the voids between graphite particles, is identified at significantly higher pore sizes and dominates the carbon black peak significantly before compacting. Separating both regions at $d_p = 0.7 \mu$ m for the graphite anode, the pore volume between 0.7 and 10 μ m, representing the pores among the active material particles, is 1.95 times the pore volume between 8 nm and 0.7 μ m, which is ascribed to the carbon black porosity. In comparison the factor is only 1.11 for the cathodes, which is a much more equalized ratio. Although the anode

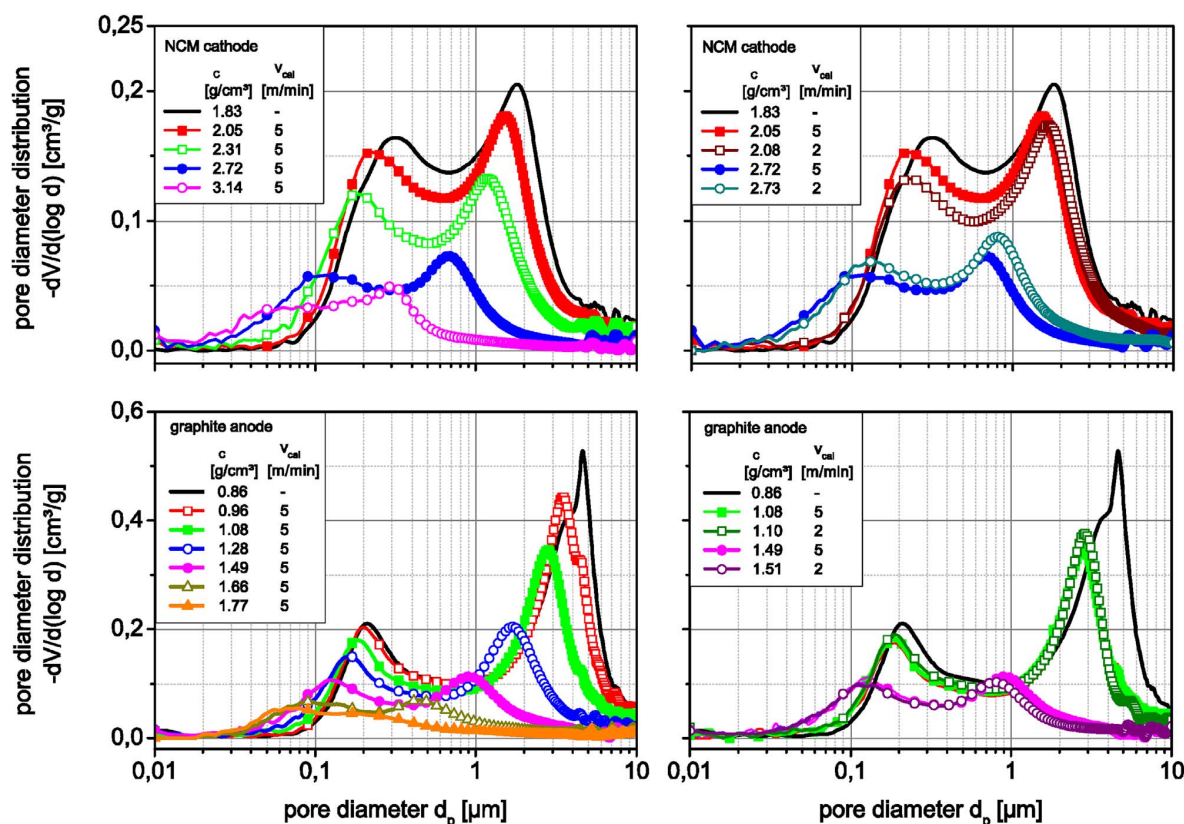


Fig. 5. Pore size distribution of NCM cathodes, uncalendered (1.83 g/cm³) ones and calendered to different coating densities (up left) and for different circumferential speeds (up right). Graphite anodes, uncalendered (0.86 g/cm³) and calendered to different coating densities (down left) and for different circumferential speeds (down right). The anodes were compacted at 5 m/min to lower porosities for comparison with the cathode.

contains more carbon black per coating volume (6.25 g/cm³ vs. 2.22 g/cm³), the cathode includes also graphite additives ($x_{50} = 3 \mu\text{m}$), which cause further pores in the carbon black peak, shift it slightly to higher pore diameters and raise the level of pores between the both peaks.

The compacting results show a general shift to lower pore sizes and specific pore volumina for cathodes and anodes, whereas the larger peak of the anode is dramatically faster decreased by compaction than the carbon black peak. One reason is the larger pore volume fraction between the graphite particles ($V_{dp} > 0.7 \mu\text{m}/V_{p,C} = 40.3\%$, vs. 25.8 % for the NCM particles) is much easier compactable and is one further factor for the significantly lower compaction resistance. The closer packing of the NCM spheres possibly leads to a higher interparticle friction resistance against the compaction, which is another reason for the higher compaction resistance, besides the earlier mentioned higher hardness of the NCM versus graphite.

Decreasing the circumferential speed to 2 m/min results in case of the anode in no significant deviation from 5 m/min (down right in Fig. 5). For the cathode there are slight deviations detectable (top right in Fig. 5), but they should not be overvalued as no global tendency to a more or less porous structure could be identified.

The coating porosity, determined by both methods, is plotted against the coating density in Fig. 6. According to Eq. (2), $\epsilon_{C,ph}$ decreases exactly linearly with ρ_C as both are calculated with the same input data of ρ_C and h_C . However, the same linear trend is also observable for $\epsilon_{C,Hg}$ versus ρ_C . Especially the $\epsilon_{C,Hg}$ values for the anodes accord very well with the $\epsilon_{C,ph}$ curve. For the cathodes a significant constant offset between the results of both methods can be seen: $\epsilon_{C,Hg}$ is approximately 8% lower than $\epsilon_{C,ph}$ as the slope is almost the same. Probably this offset arises from closed pores like inner voids of the NCM

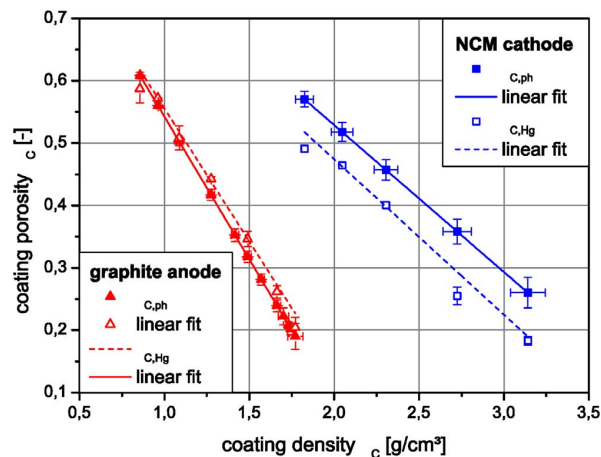


Fig. 6. Coating porosity calculated from the density or Hg porosimetry of graphite anodes and NCM cathodes, uncalendered and calendered to different coating densities at 5 m/min circumferential speed.

particles, which cannot be detected by the Hg porosimetry. Such voids are visible in SEM images of cross sections of NCM particles but not in graphite (Fig. 7). The voids are not compacted through the calendering process.

3.1.3. Porosity-based considerations

The coating porosity determined by both methods is plotted against the line load in Fig. 8. Considering the porosity instead of the coating

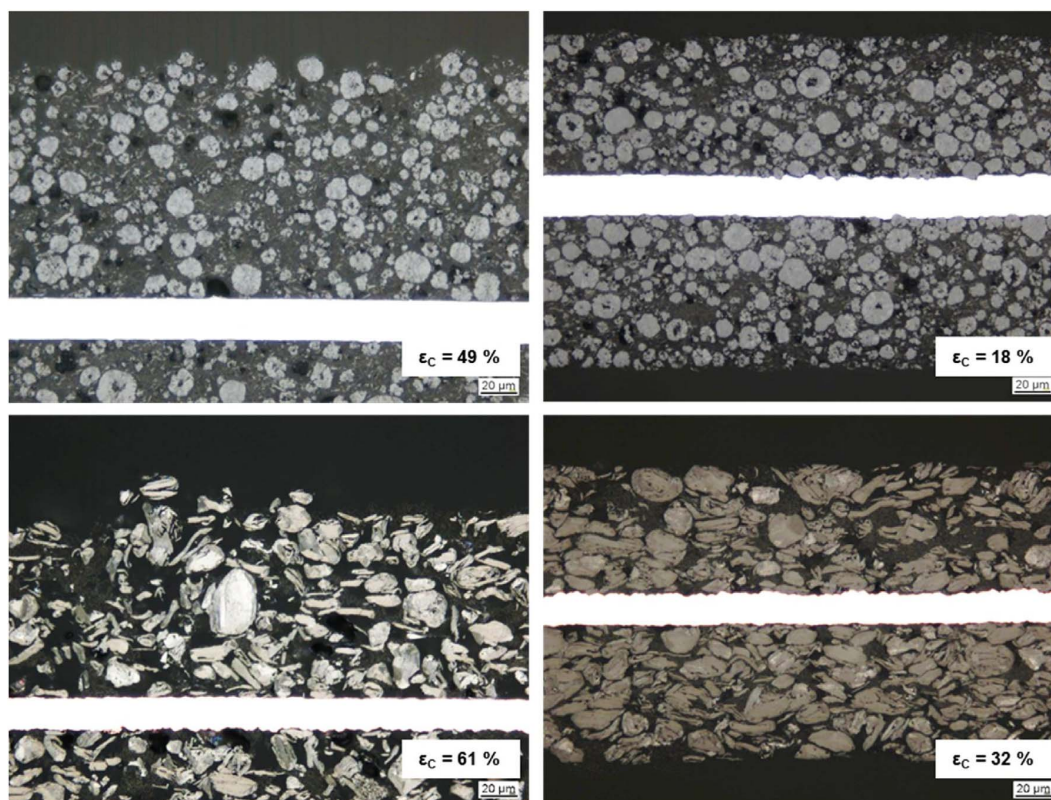


Fig. 7. SEM images of cross sections of NCM cathodes (up) and graphite anodes (down), uncompact (left) and highly compact (right). Innerparticle voids are visible in the NCM particles. The thickness of the uncompact electrodes (left) is too high to depict in total at the chosen resolution.

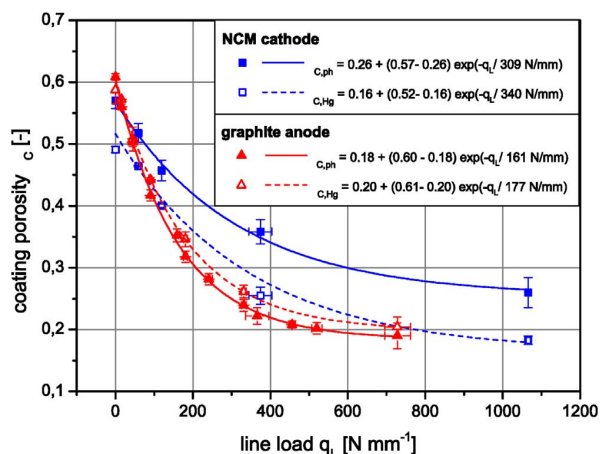


Fig. 8. Decrease of the coating porosity of graphite anodes and NCM cathodes by calendaring at 5 m/min circumferential speed and varied line loads. The anodes were compacted stronger than in Table 2 and Fig. 4 for comparison of the anodes and cathodes in the whole porosity ranges, which explains different values.

density the differences in calendaring behavior become even more obvious and comparable. The porosities of the anode and cathode decrease exponentially with the applied line load, converging towards porosity minima. The data are fitted analogous to Eq. (4).

The approximation equations are depicted in Fig. 8 as well. The extrapolated porosity minimum of the anode based on the physical density is about 18% and based on the measurements by Hg porosity is about 20%. These results equal the extrapolated density maximum of 1.74 g/cm³ for anodes, compacted only to lower densities (compare

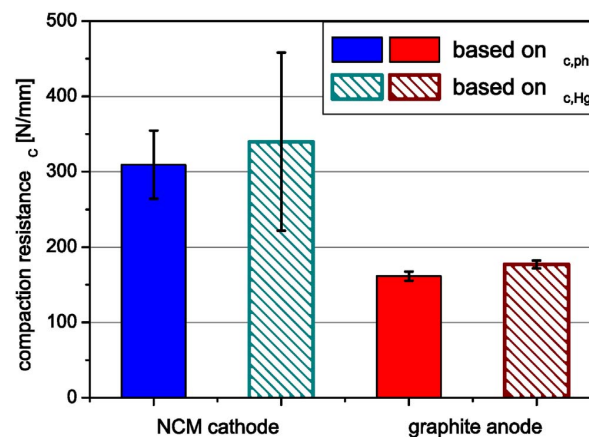


Fig. 9. The compaction resistance γ_C at $v_{cal} = 5$ m/min for different electrodes regarding different porosity determination methods. The anodes were compacted stronger than in Table 2 and Fig. 4 for comparison of the anodes and cathodes in the whole porosity ranges, which explains different values.

Table 2), which corresponds to 19% porosity, based on the physical density.

The resulting compaction resistances γ_C are supplementary compared in Fig. 9. As expected, both cathode-related γ_C values (porosimetry determined and physical density determined) are the same. Using the porosities from mercury intrusion measurement, a quite similar γ_C , in spite of the deviating porosity scale, is obtained. The higher deviation of the cathode compared to the anode is explainable, since less data points are used. Using a higher amount of data points, in a

wide range, the results show almost no deviation (see Fig. 9, anode). However, by investigating the porosity changes with increasing line load, the high difference in the compaction behavior between both electrodes becomes even more clearly. The NCM cathode has a larger resistance against its compaction, quantifiable by γ_C , manifesting in a more gradual convergence to its maximal density, respectively minimal porosity.

4. Conclusions

The examination of the relation between the applied line load and the achieved coating density and porosity revealed an exponential correlation. A mathematical description was presented (model Eq. (4)), which besides the starting and end point of compaction contains one parameter, qualifying the converging course to a density maximum or porosity minimum, called compaction resistance γ_C . This characteristic parameter represents the compaction resistance of the electrode coating, which is identified to be highly dependent on the used materials and formulations and the pore structures developed in the coating, but less dependent on the roller speed. In future work, the effect of different materials, formulations (e.g. binder and additive content), mass loads and operating parameters (like roll temperature) on the compaction resistance will be determined. Above this, to find an alternative way of determining the end point of compaction (maximal density or minimal porosity) instead of extrapolation of this equation, would be a complementary approach. Furthermore, it may be illuminating to examine the calendaring effect on the mechanical properties of electrodes to learn more about the deforming impact of the compaction process itself.

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