Impacts of Variations in Manufacturing Parameters on Performance of Lithium-Ion-Batteries

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Cell performance of lithium-ion-batteries (LIB) can be tailored to particular hybrid or full electric vehicle applications by targeted adjustment of manufacturing parameters. Furthermore there is a large number of cathode material compositions which can be used. Knowing the correlations between these parameters, electrode structures and cell performance is important to reach the high requirements posed by electromobility. Within this study, impacts of essential manufacturing parameters, being active material mass loading, calendering stress load and carbon black content on the cell performance were investigated for two different, promising cathode materials. For NMC and LMO, the respectively highest calendering stress load and carbon black content yielded the best performance as losses due to poor electronic conductivity were reduced. The active material mass loading rather influenced the ratio between specific energy and specific power. Finally two optimally performing parameter configurations could be identified which were, depending on the required application: NMC with high mass loading and LMO with medium mass loading; in both cases the highest calendering load and carbon black content were applied. An analysis of statistical reproducibility dependent on various parameter configurations was carried out as well. A significant improvement of reproducibility could be achieved by increase of calendering stress load.

Lithium-Ion-Batteries (LIB) are the technical bottleneck of electric vehicles, hindering them to become competitive to combustion engine powered cars in terms of costs, driving range and recharging time. To improve their performance, it is important to understand battery physics entirely and the impact of manufacturing parameters on it. As the electrodes are complex particle-pore-systems with several materials involved, there is a large number of parameters which can be varied in order to optimize the battery with respect to the required performance targets. An analysis of parameter tuning for high power applications at especially high C-rates, e.g. for fast charging applications can be found in the work of Du Pasquier et al.,[1] where up to 80C could be realized with a $Li_4Ti_5O_{12}$ vs. $LiMn_2O_4$ cell by optimizing particle size, electrode formulation and the ratio of active material mass loadings between anode and cathode. Due to the highly non-linear physico-chemical correlations within the electrodes, simulation-supported parameter analysis and optimization show to be a powerful complementary tool for battery design.[2–4] Röder et al.[5] showed with the aid of simulation that variations in size distribution of active material particles affect performance and lifetime. Understanding correlations between mixing, dispersing and calendering parameters and the particle-pore-structure are important, in order to enhance battery performance for individual material compositions.[6–11] Depending on structural properties, causes of performance limitations may vary between insufficient lithium diffusivity and electronic resistances.[12,13] Especially for electromobility applications, the choice of active material mass loading, which defines the electrode thickness, is important because it essentially influences the ratio between specific energy and specific power of a battery[14–16] where the former impacts on driving range and the latter impacts on acceleration of a vehicle. Influences of calendering and conductive additives, e.g. carbon black on the electrochemical cell performance have been investigated by Bockholt et al.[17] They found that calendering exerts various effects on the electronically conductive pathways, whereby it depends on the structure of carbon black particles if these effects are beneficial or destructive for cell performance. In the case of LMO cathodes calendering degrees of about 25 % showed to be an optimal compromise between C-rate performance and long term cycling.[18] For optimization of LIB properties, the choice of cathode material is essential as well. One promising material composition for automotive applications is $LiMn_2O_4$ (LMO) due to its relatively low cost, non-toxicity and high abundance.[19–21] It can also be considered as safer than established cobalt based compositions due to its lower extent of self-heating.[22] Another promising composition is $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC) due to its high specific capacity and moderate cost compared to other conventional cathode materials, such as $LiCoO_2$.[20,23] Variations of the distinct parameters mentioned above are combined and their impacts on performance and statistical reproducibility are investigated within this work. The resulting pouch cells were manufactured and electrochemically characterized by capacity measurement and C-rate tests. The variation parameters focused in this study are active material mass loading (ML), mass fraction of carbon black, degree of calendering and comparison of two cathodic active materials (NMC and LMO). These parameters are of particular interest as they can be used to design a battery with respect to optimal specific energy or specific power which is essential for automotive batteries; high specific energy is more important for application in hybrid electric vehicles (HEVs), whereas high specific power is more important for the use in full electric vehicles (FEVs). To examine statistical reproducibilities, four cells per parameter configuration were assembled.

Experimental

Electrode manufacturing and parameter variations.—For all electrodes, carbon black (CB) was used as conductive additive and polyvinylidenefluoride (PVDF) was chosen as binder. Active materials (AM) are $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ for NMC electrodes and $LiMn_2O_4$ for LMO electrodes, respectively. All cathodes were processed with N-Methyl-2-pyrrolidone (NMP) as solvent. All suspensions were prepared using a planetary mixer (PMH10, NETZSCH-Feinmahltechnik GmbH). Firstly, the powdery components were dry-mixed for homogenization with low energy input and secondly, after adding the solvent, the speed of the fast rotating toothed disk stirrer was increased to 2000 min^{-1} and all components were dispersed for 60 minutes in the solvent. The solids content while dispersing was set to 55 % and 60 % for NMC and LMO, respectively, and the suspension was degassed for at least 15 minutes at the end of the process. All suspensions were coated on the current collector (20 μm aluminum foil for cathodes and 10 μm copper foil for anodes) using a technical scale continuous coating device with 2 m/min coating speed and dried subsequently in a three stage convective drying process (LabCo, Kroenert GmbH and Drytec) for 3 minutes (80°C, 100°C and 120°C; 1 minute each). The calendering of the electrodes was carried out using a two roller compactor in pilot scale (GKL

Table I. Experimental plan depicting the investigated parameter configurations. Included are recipes with low and high carbon black content, respectively; the former involves a carbon black to binder ratio CB:B = 1, whereas for the latter CB:B > 1 holds due to the reduced binder content. Furthermore, parameter variations in form of low, medium and high active material mass loading and low, medium and high levels of volume reduction by calendering for both cathode materials were applied, respectively.

Electrode	Active material mass – %	Carbon black (CB) content and CB:B ratio mass – %	Binder (B) mass – %	Active material mass loading (ML) mg cm^{-2}	Calendering configuration in terms of volume reduction low/med/high %	Theoretical area capacity mA h cm^{-2}
Cathode recipe 1	NMC	low content:4	PVDF	9.00(low)	0/10/22	1.40
	92		4	12.00(med)	0/10/22	1.85
		CB:B ratio = 1		15.00(high)	0/10/22	2.30
Cathode recipe 2	NMC	high content:5.88	PVDF	9.00(low)	0/10/22	1.40
	90.20		3.92	12.00(med)	0/10/22	1.85
		CB:B ratio > 1		15.00(high)	0/10/22	2.30
Cathode recipe 3	LMO	low content:4	PVDF	13.00(low)	0/15/30	1.40
	92		4	17.20(med)	0/15/30	1.85
		CB:B ratio = 1		21.60(high)	0/15/30	2.30
Cathode recipe 4	LMO	high content:5.88	PVDF	13.00(low)	0/15/30	1.40
	90.20		3.92	17.20(med)	0/15/30	1.85
		CB:B ratio > 1		21.60(high)	0/15/30	2.30
Anode	Graphite	content:5	CMC : SBR	3.83(low)	10	1.40
	90		2.5 : 2.5	5.10(med)	10	1.85
		CB:B ratio = 1		6.38(high)	10	2.30

400 MS, Saueressig GmbH & Co. KG). The production parameter sets chosen for investigation in this study are listed in Table I. For both cathode materials NMC and LMO, a graphite anode was used as counter electrode, respectively. A reference recipe containing 5.88 mass-% carbon black and a carbon black to binder ratio of CB:B > 1 was taken which is based on best practice from previous experiments. As carbon black is an inactive material which is not able to intercalate lithium, it would be advantageous to reduce carbon black content to achieve an improvement of specific energy. Therefore, a recipe with a low carbon black content of 4 mass-% and CB:B = 1 was also chosen. The performance tests presented in this study should show if the reduction of carbon black leads to losses due to a deterioration of electronic conductivity, on the other hand. Three different active material mass loadings (ML) were produced for each recipe. The lowest mass loadings for the respective electrodes were chosen in order to yield electrode thicknesses suitable for high specific power applications, e.g. HEVs, whereas the highest mass loading should represent electrode thicknesses suitable for high specific energy applications, e.g. FEVs. For each cathode parameter configuration, three calendering levels were applied. The lowest level was non calendered for both cathode materials, the medium level was 10 % volume reduction for NMC and 15 % volume reduction for LMO. The highest volume reduction was 22 % for NMC and 30 % for LMO and this was based on best practice from previous experiments.[6,18] LMO electrodes are known to require high calendering degrees to achieve acceptable rate performance within the cells,[18] thus they were stronger compressed than the NMC electrodes. For all used cathodes, the related anode was calendered to a level of 10 % volume reduction.

Assembly of test cells and their characterization.—The in-house produced electrodes were punched to assemble single layered pouch cells with an area A=25 cm^2. In previous experiments, these cells were proven to realize stable and reproducible performance where impacts of electrode parameter variations can be investigated without disturbance of stacking effects. As electrolyte EC:DEC 3:7, 1M $LiPF_6$ and as separator CELGARD 2320 were used. Four cells were assembled for each parameter configuration to ensure a minimum of statistical certainty. electronic resistances of electrode samples were measured using a Zwick Z010 material testing machine; the sample was positioned between two stamps which were then pushed together with a force of 40 N and a current of 10 mA was passed through it, corresponding to the measurement routine presented by Westphal et al.[13] Electrode thicknesses were measured to calculate the specific electronic resistance with a Mitutoyo Digimatic ID-C tactile gauge with a measurement accuracy of ± 1 µm. After cell assembly and 24 hours of rest time, formation was carried out with two constant current (CC) cycles at 0.05C where the respective current was calculated based on the theoretical capacities (Table I) of the active materials given in the respective material data sheets. To minimize inaccuracies in the derived currents for the C-rate tests due to deviations between theoretical and real capacities, the latter were measured at the end of the second formation discharge process; these real capacities were taken to define the currents for the C-rate tests which consisted of discharge curves measured at 0.2C, 0.5C, 1C, 2C and 5C. Charging was done at 0.2C with CC and each cycle was repeated three times to ensure statistical reproducibility. For formation and C-rate test the chosen lower and upper cutoff voltages for cells with both cathode materials were 2.9 V and 4.2 V, respectively; all performance measurements were carried out in a temperature chamber at 20°C.

Analytical methods.—For better comparison of the effects of variations in calendering, carbon black content and cathode material type on cell performance, discharge capacities are displayed normalized to cathodic active material mass. For comparison between various mass loadings, this reference was considered unsuitable as it would neglect that respective anodic mass loadings also have to be adjusted to keep the battery balanced and it would also neglect the beneficial tendency of higher mass loadings due to current collector and separator dimensions which do not have to be increased. This improves the active to inactive material mass ratio. Therefore capacities for evaluation of mass loading impacts were normalized to the sum of the masses of both electrodes, electrolyte, current collectors and separator, similar to the work of Appiah et al.[4] Cell case mass of the one-layered pouch cells used in this study were omitted as their mass fraction is not equivalent to the one of cell cases in automotive format cells. For derivation of the quantities needed to create the Ragone plots, the measured mass-related discharge capacities were transformed into specific energy values by multiplication with the time-average discharge cell voltage. This was calculated as the mean value of discrete voltage measurement points during discharge for each C-rate and parameter configuration, respectively. Then corresponding values for specific power were derived by dividing the specific energy values by the respective discharge times for the applied C-rates. Standard deviations were calculated for discharge capacities at each C-rate. Deviations among the three repetitions per C-rate in each cell were negligibly small; therefore mean values of the three capacities were

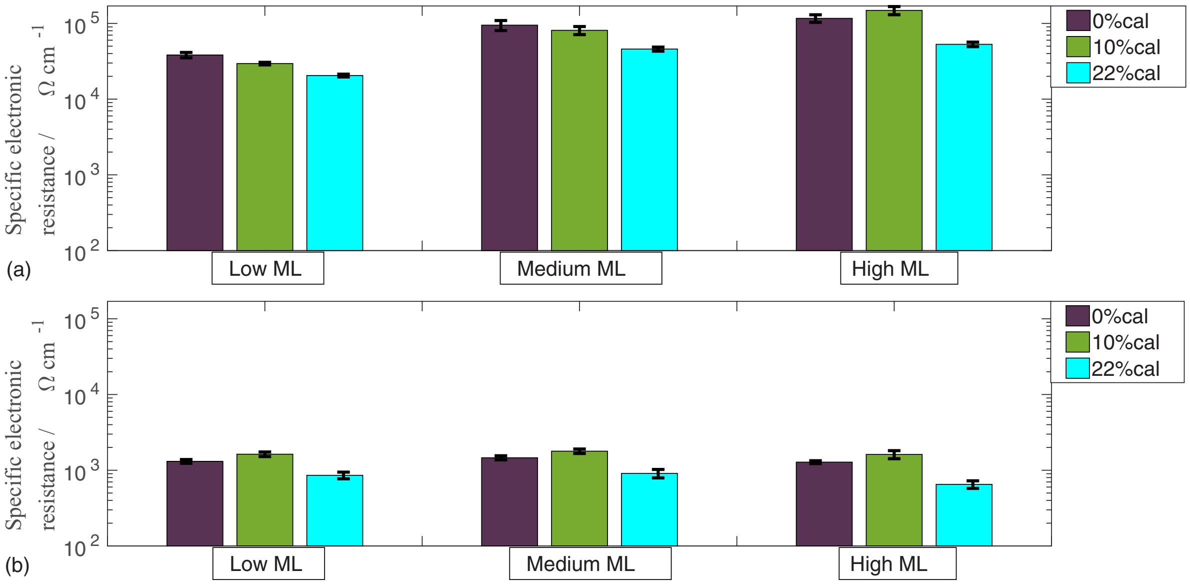

Figure 1. Electronic resistances normalized to electrode thickness of NMC cathodes with standard deviations for various mass loadings (ML) and calendering stress loads. The resistances are depicted for both carbon black recipes, respectively, being low carbon black content (CB = 4 mass-%) with carbon black to binder ratio (CB:B = 1) (a) and high carbon black (CB = 5.88 mass-%) content with CB:B > 1 (b).

used without further consideration of statistical deviations. However, significant deviations occurred between discharge capacities of the four respective cells which were produced with the same parameter configurations. Performance curves given in the Results section are related to the respectively best functioning cell out of the four cells with same parameter configurations. A separate discussion about standard deviations, reproducibility and their dependencies on manufacturing parameters will be given in the subsection on correlations between statistical reproducibility and electrode design. Additionally, for the analysis of calendering impacts, to quantify performance deteriorations because of too low applied calendering stress loads, dimensionless quotients of specific discharge capacities of cells with medium to low calendering configurations divided by the respective specific discharge capacity of the high calendering configuration were derived, respectively for various cathodes recipes and mass loadings.

Results and Discussion

In this chapter the impacts of the varied parameters on cell performance will be discussed. The evaluation of calendering impacts, the comparison between NMC and LMO and the investigation of impacts by simultaneous reduction of carbon black content and carbon black to binder ratio, are carried out based on the experimentally determined specific discharge capacities at various C-rates. Impacts of electrode mass loadings are discussed with the aid of Ragone plots. Furthermore, significant correlations between statistic reproducibility and parameter variations will be pointed out and measured specific electronic resistances of NMC cathodes will be shown to support the physical interpretation of parameter impacts. Figure 1 gives an overview on the electronic resistances and will be discussed in context with the experimental results of electrochemical performance in the following chapters. The specific electronic resistances were measured at samples of NMC cathodes for all manufacturing parameter variations in order to evaluate the respective impacts of calendering stress load, active material mass loading and the simultaneous adjustment of carbon black content and carbon black to binder ratio, on electronic conductivity. Previous investigations[3] showed that malfunctioning of non calendered cathodes with low carbon black content and CB:B = 1 was mainly caused by worse effective electronic conductivity which resulted in a limitation of electron transport in the cathode at high C-rates. The specific electronic resistances of NMC cathodes measured in this study confirm this finding as they are significantly lower at high carbon black (CB) contents and CB:B > 1 for all mass loading (ML) configurations (Figure 1). Further reductions of specific electronic resistances were achieved by applying the highest calendering stress load of 22% volume reduction.

Calendering impacts on C-rate performance.—The impact of calendering on specific discharge capacity at various C-rates is analyzed in the following. Figures 2 and 3 show the impact for NMC and LMO, respectively. Both materials have in common that best performances were achieved with the highest applied calendering stress loads. Towards high C-rates the differences of specific discharge capacities among various calendering configurations increased which can be attributed to increased overpotentials due to the increased discharge currents. The performance plots for all calendering levels and the entire range of C-rates are shown for cathodes with high carbon black content, CB:B > 1 and medium mass loadings exemplarily. The here depicted tendency that medium to low calendering configurations performed worse than the high calendering configurations was found for all other parameter configurations as well. Whereas, the amount of performance deterioration of medium and low calendering configurations with respect to the performance of high calendering configurations varied. This is shown for other active material mass loadings or carbon black contents for NMC in Figures 2b, 2c and for LMO in Figures 3b, 3c, respectively. In these plots, the specific discharge capacities at medium and low calendering stress loads are given, normalized to the respective specific discharge capacities at high calendering stress loads. For NMC cathodes, this depiction suggests that at low C-rates, here at 0.5C variations of active material mass loading are relatively insensitive to calendering impacts (see Figure 2b), whereas the reduction of carbon black content leads to a strong decrease of specific discharge capacity even at 0.5C when relatively small calendering stress loads, here ≤ 10%, are applied. Taking the increase of electronic resistances into consideration which were measured for cathodes with low carbon black contents, CB:B = 1 and medium to low calendering configurations (Figure 1), these results confirm the findings of Lenze et al.[3] and Bockholt et al.[17] that additional electronically conductive pathways can be generated by application of high calendering stress loads; this leads to an enhancement of cell performance. Parameter variations which have a rather small but still significant impact on cell performance can be identified at high C-rates. At 5C where the calendering impact is even observable for NMC cathodes with high carbon black contents and CB:B

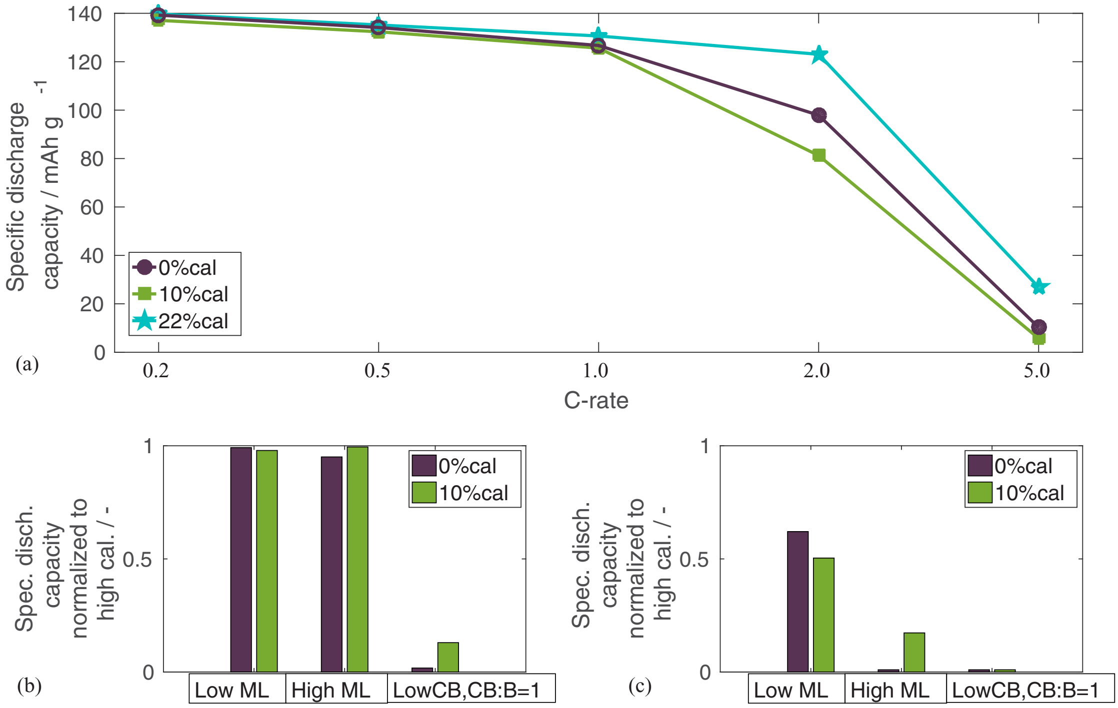

Figure 2. C-rate performances of variously calendered NMC cathodes with medium ML and high CB contents, CB:B > 1 (a). Additionally, remaining specific discharge capacities of the NMC cathodes manufactured with medium and low calendering stress loads are shown, with respect to the specific discharge capacity of cathodes with high calendering stress load at various parameters at 0.5C (b) and 5C (c). In (b) and (c) holds that for the depicted ML (low and high) variations, high CB contents with CB:B > 1 were chosen and for the depicted CB (low, CB:B = 1) variation, medium ML was chosen, so that the parameter configuration from (a) can be taken as reference and (b) and (c) can be compared to it as single parameter variations.

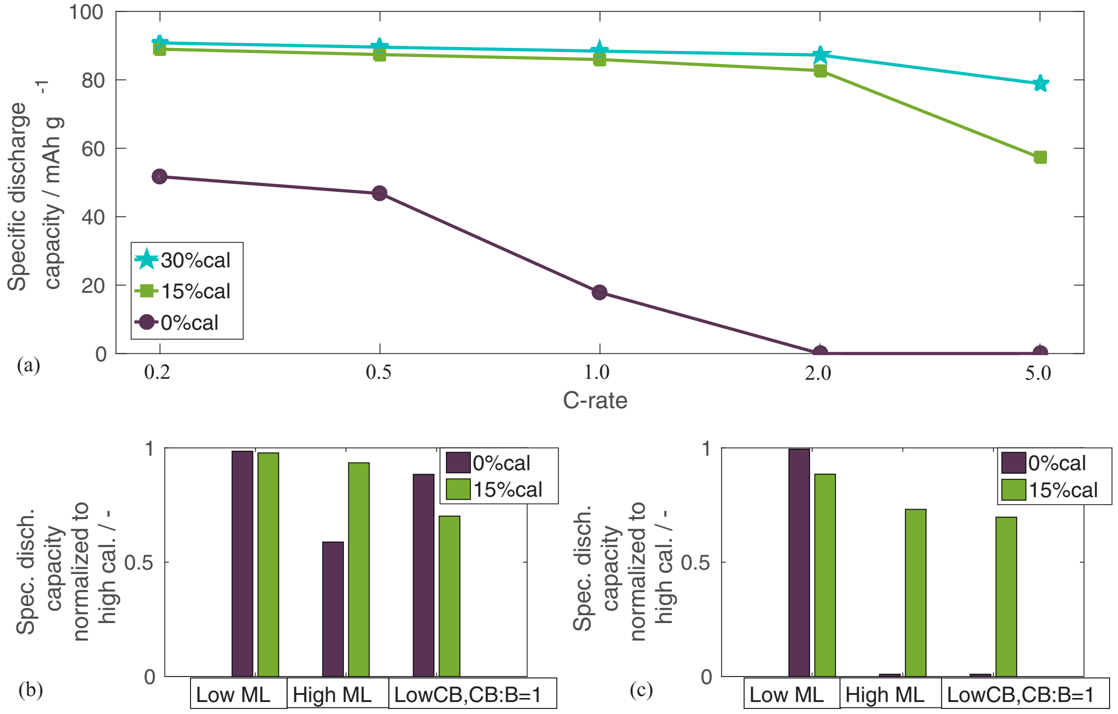

Figure 3. C-rate performances of variously calendered LMO cathodes with medium ML and high CB contents, CB:B > 1 (a). Additionally, remaining specific discharge capacities of the LMO cathodes manufactured with medium and low calendering stress loads are shown, with respect to the specific discharge capacity of cathodes with high calendering stress load at various parameters at 0.5C (b) and 5C (c). In (b) and (c) holds that for the depicted ML (low and high) variations, high CB contents with CB:B > 1 were chosen and for the depicted CB (low, CB:B = 1) variation, medium ML was chosen, so that the parameter configuration from (a) can be taken as reference and (b) and (c) can be compared to it as single parameter variations.

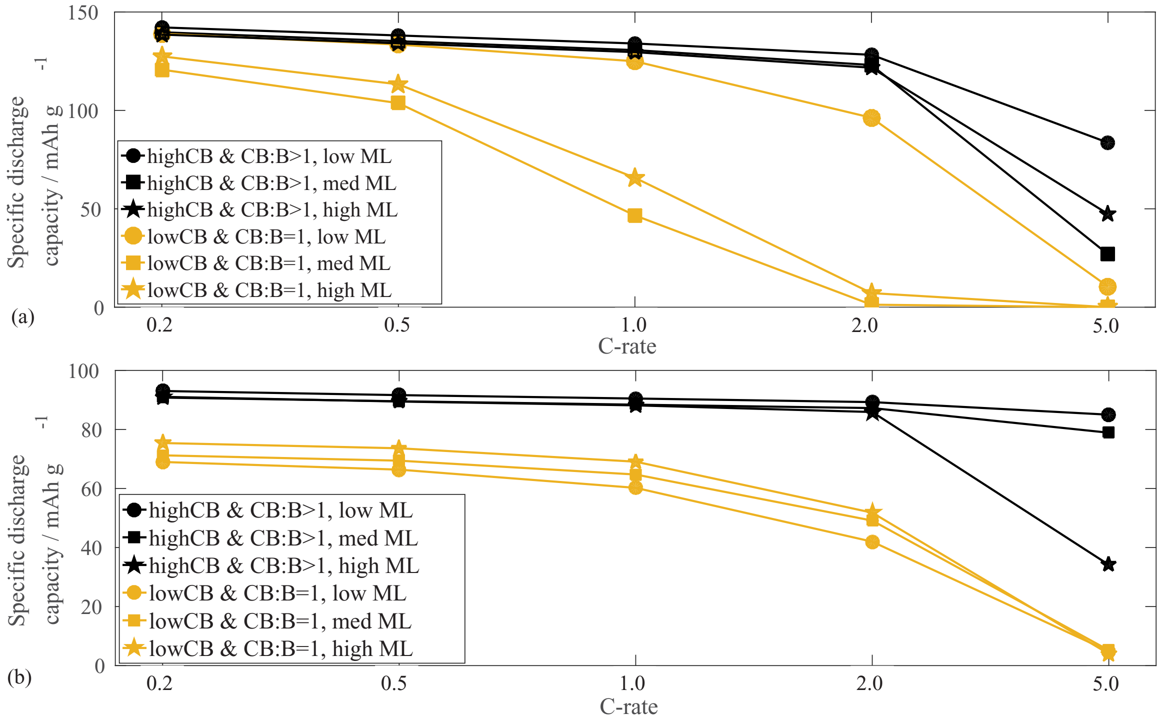

Figure 4. Comparison of specific discharge capacities over C-rates with low carbon black contents (4 mass-%), CB:B = 1 (light curves) and high carbon black contents (5.88 mass-%), CB:B > 1 (dark curves) for NMC (a) and LMO (b) cathodes, respectively, at the high calendering configuration.

> 1, an additional correlation with active material mass loading occurs (see Figure 2c). At low mass loadings the deterioration of specific discharge capacity for medium and low calendering configurations is about 50% compared to the configuration with high calendering stress load. However, this deterioration is still relatively small compared to the cells with high mass loadings where specific discharge capacity even approaches 0 mAh/g for non calendered cathodes. The higher sensitivity of high mass loadings to calendering impacts compared to low mass loadings is physically reasonable because the missing electronically conductive pathways in cathodes of medium to low calendering configurations make the cathode become the most limiting cell component for the discharge performance, with higher overpotentials for thicker cathodes, i.e. higher mass loading. There is no reproducible trend observable for NMC if the low calendering configuration is causing even more performance losses than the medium one. Rather it has to be concluded that significant performance losses due to missing electronically conductive pathways occur for calendering stress loads $\leq$ 10% in general. This is different for LMO cathodes; Figures 3, 3b and 3c show that the main part of performance loss occurs between the medium and the low calendering configuration. Similar to NMC, the calendering impacts in LMO cathodes are relatively small when low active material mass loadings are applied. However, for LMO at 0.5C not only a reduction of carbon black content but also a high mass loading shows significant calendering impacts on performance already (see Figure 3b). At 5C it becomes obvious that the variation between medium and low calendering configuration causes significantly higher performance losses than an increase of mass loading or a reduction of carbon black content (see Figure 3c). In general discharge capacities for cells assembled with LMO cathodes show a lower gradient over C-rates than NMC which reflects their better high power ability than NMC. This does obviously only hold if electrodes are sufficiently calendered. These results confirm not only that for cathodes with low calendering configurations, limitations of C-rate performance are dominated by electronic resistances as discussed above. Also the finding from previous investigations of Lenze et al.[3] and Schilcher et al.[18] that ionic conductivity which is assumed to be deteriorated by calendering is not significantly affecting the battery performance or at least it has only a minor impact, within the relevant calendering range up to 22%(NMC)/30%(LMO) of compaction and with the chosen other manufacturing parameters. The study of Gallagher et al.[14] supports the assumption that a limitation by ionic conductivity begins at considerably thicker electrodes where the electrode thickness is equivalent to the quantity of active material mass loading. According to Gallagher et al. these limitations of ionic conductivity occur at a thickness of 154 µm or higher. The cathodes manufactured for the high mass loading configurations in this study were still significantly thinner; they had after compaction for the respective high calendering configurations electrode thicknesses of about 70 µm for NMC and 103 µm for LMO which for the given electrode and porosity is too low for limitations by ionic conductivity. The electrode porosity which is reduced by calendering is also assumed to cause a significant deterioration of ionic conductivity when it is reduced too much because this leads to an increase of tortuosity of ionic transportation pathways. The cathodes where limitations due to ionic conductivity occurred which were investigated by Gallagher et al., had porosities within a range 0.32–0.40, whereas the porosities calculated for the cathodes analyzed in this work were significantly higher, in the range 0.45–0.55. This also confirms the assumption that the calendering stress loads applied on cathodes in this work were too low to affect ionic conductivity significantly. Another advantage of calendering is that the energy density is increased by the induced compaction which can be analyzed with the aid of Ragone plots, normalized to electrode volume.

Impact of carbon black content.—In the following we will investigate in detail the effect of simultaneous reduction of carbon black content from 5.88 to 4.00 wt-% and carbon black to binder ratio from CB:C > 1 to CB:B = 1, as a low content of inactive materials may increase energy density. The cathode recipes with high carbon black content (5.88 wt-% and CB:C > 1) were chosen as a best practice reference which showed good performance in previous experiments. Aiming to enhance energy density in this experiment, cathodes with low carbon black content (4.00 wt-% and CB:B = 1) were tested for comparison. As shown in Figure 4, cathodes with the high

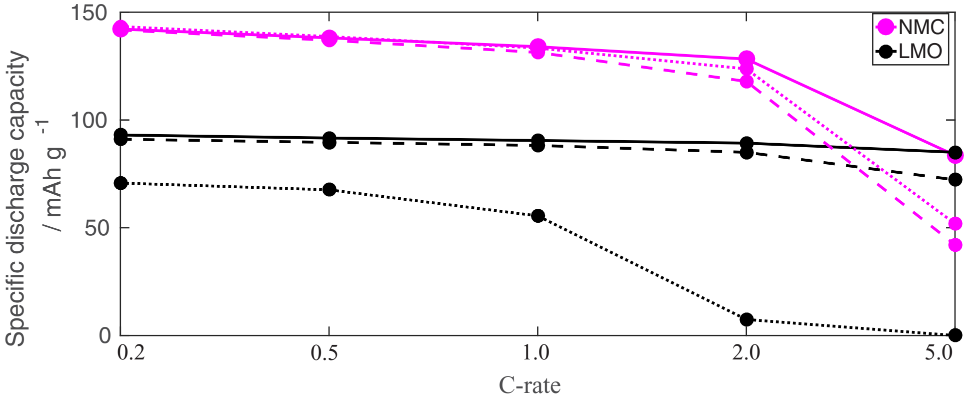

Figure 5. Specific discharge capacities for NMC and LMO at high CB content, CB:B > 1, low ML as function of C-rate and calendering configuration: non calendered (dotted lines), medium calendering stress load (dashed lines) and high calendering stress load (solid lines).

carbon black content and CB:C > 1 provided higher specific discharge capacities with respect to cathodic active material mass throughout all mass loadings at the high calendering configuration. This holds for both cathode materials, NMC and LMO. For low to medium calendering stress loads, the performance of cathodes with low carbon black content and CB:B = 1 decreased even more and thus were not competitive at all. The results show also that for NMC cathodes, a deterioration of performance by reduction of carbon black content and CB:B ratio occurs, especially at higher C-rates. This can be attributed to worsened electronic conductivity correlating with the significantly increased electronic resistances which were measured for all NMC cathodes with low CB content and CB:B = 1 (Figure 1). It is assumed that not only the carbon black content but also the structure and homogeneous mixture of the carbon black-binder matrix impacts on the electronic conductivity which can be influenced by the CB:B ratio. A too low CB:B ratio may cause carbon black fractions which are entirely covered with binder and therefore isolated from the electronically conductive network.[17] Only for low mass loadings and low C-rates < 1C the cathodes with low carbon black content and CB:B = 1 show similar performance as ones with high CB content and CB:B > 1, which makes them only to a limited extend suitable for automotive applications. In the work of Martínez-Rosas et al.[24] load profiles for urban and suburban operation of electric vehicles are presented which show that discharge currents ≥ 0.5C for urban operation and ≥ 1C for suburban operation are required. The cathodes with low carbon black content and low CB:B ratio may therefore be attractive for non-automotive applications, e.g. consumer electronics where batteries can be operated at even smaller C-rates. For LMO the reductions of carbon black content and CB:B ratio are disadvantageous in general (Figure 4b).

Performance comparison of NMC and LMO.—Many investigations of particular active materials for cathodes can be found in literature but there are rather few studies, like the one of Julien et al.[19] which compare electrochemical performance of several active materials to each other. Therefore, within this chapter characteristic advantages and disadvantages of the two investigated cathode materials will be analyzed. Comparison of Figures 2, 3 and 5 reveals characteristic differences for the C-rate behavior between NMC and LMO: NMC has higher specific discharge capacities at low C-rates and LMO shows higher specific discharge capacities at higher C-rates. Indeed, an intersection of NMC and LMO performance curves can be observed for most calendering and mass loading configurations. In the case of high CB content and low ML, exemplary shown in Figure 5, the intersections are between 2C and 5C for medium calendering and at 5C for high calendering. For non calendered cathodes, no intersections can be identified as for LMO cathodes the specific discharge capacity over C-rate drops to 0 mAh/g before an intersection occurs. Intersections which could not be attributed to a particular C-rate as in the medium calendered case, were estimated by linear interpolation. The intersections of performance curves appear at different C-rates for the various parameter configurations. An overview on intersections of all configurations is given in Figure 6. If a battery is operated mainly at C-rates below the intersection it is advantageous to choose NMC as cathode material because it gives higher capacities. Whereas for operation above the intersection, LMO cathodes reach higher specific discharge capacities and can therefore be seen as preferable, at least if other aspects as cycling stability are not considered. In general two trends can be observed. First, for cathodes with low CB content and CB:B = 1 the turning points are either relatively low at 1C or below, or they do not even exist due to the poor performance of NMC

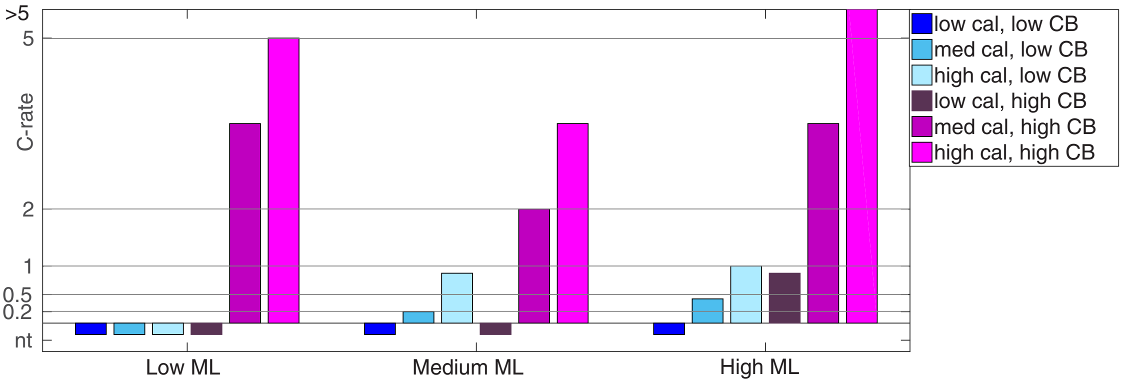

Figure 6. Performance curve intersections of NMC versus LMO for several parameter configurations.

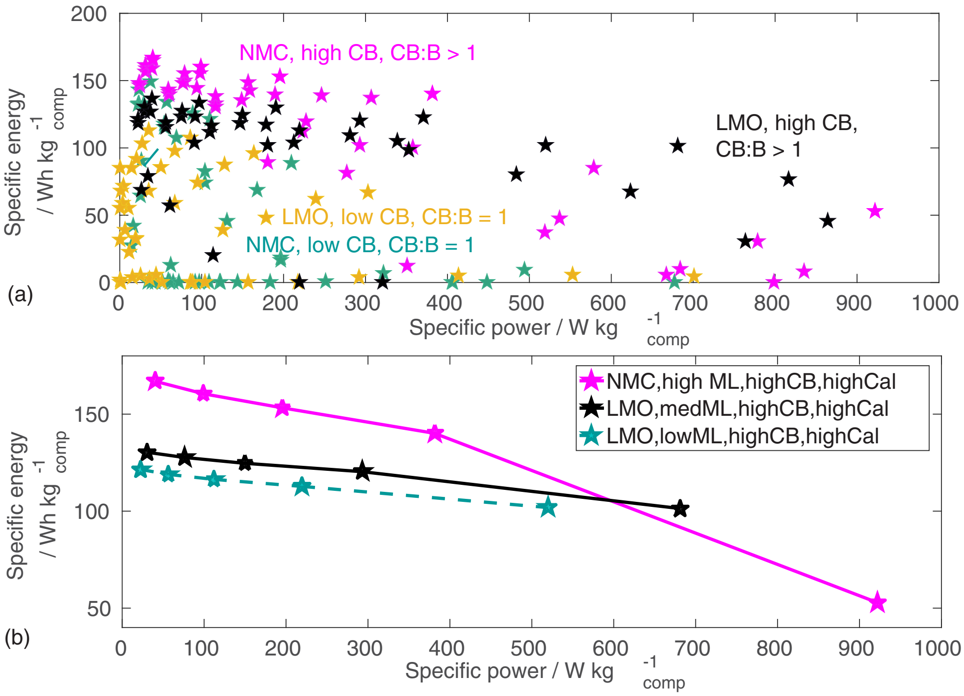

Figure 7. Ragone plots including specific energy and specific power values of all investigated parameter configurations and C-rates (a) and analysis of optimal parameter configurations for battery operation under high specific energy and high specific power emphasis, respectively (b). Specific quantities were derived by normalization to the compartment mass which contains electrode, electrolyte, current collectors and separator. Electrodes with low CB content and CB:B $= 1$ are not considered in this operation oriented evaluation as their performance is too poor.

cathodes which is depicted by column entries denoted by nt (nt: no turning point which means no intersection of performance curves). Second, the higher calendering stress load is applied the further gets the intersection shifted to higher C-rates. This can be attributed to the general improvement of performance by calendering for both materials but the positive impact by calendering is proportionally higher for NMC than for LMO. In the case of high calendering, high ML and high CB content no intersections could be found for C-rates up to the highest C-rate which was measured in this study. More detailed evaluation, e.g. of intersections which may occur at C-rates $\geq$ 5C or which lie between two C-rates presented in this study, require further measurements and is out of scope of this work. An essential characteristic which distinguishes NMC from LMO regarding respective performances is that LMO shows lower specific discharge capacities at minor C-rates of 0.2 to 0.5 which can be attributed to its lower theoretical capacity compared to NMC. This yields that for assembly of cells with equal energy content, the required active material mass loading of LMO has always to be higher than for NMC. An advantage of LMO, is the good performance at higher C-rates ($\geq$ 1C); overpotentials seem to be significantly lower than for NMC which may be a result of the material structure. It is assumed that NMC with its layered structure enables only for two-dimensional lithium intercalation, whereas LMO with its spinel structure can intercalate lithium from three spacial directions which speeds up the electrochemical kinetics. The improvement of high C-rate capability due to change from layered to cubic spinel structure was presented in the work of Song et al.;[25] their results support the hypothesis that diffusive lithium transport within the active material particles is indeed improved by a spinel structure. Also Julien et al. pointed out the fast lithium diffusivity in the three dimensional LMO structure.[19] This is especially interesting in the context of the here depicted experiments as it shows that for high C-rate applications not only the electronic conductivity or in the case of too high calendering stress loads the ionic conductivity in the electrolyte need to be considered as limiting processes for cell performance, but also the diffusivity of lithium within the particles. The advantages of its spinel structure make LMO an interesting material for high C-rate applications, e.g. hybrid electric vehicles. However, other properties like cycling stability also have to be considered for a funded decision.

Mass loading impact and optimal parameters.—The measured performance data of all parameter configurations at various C-rates were converted into a Ragone plot shown in Figure 7a. Energy and power are mapped both after normalizing to the compartment (comp) mass. For the investigation of impacts of active material mass loading on cell performance, normalization to the compartment mass is more reasonable than to active material mass. This is because the thicknesses of the porous electrodes and thus also the volume of electrolyte increases with increasing mass loading; however, the thickness of current collectors and separator stays constant. Therefore normalization to active material mass would neglect the beneficial effect of electrodes with high mass loadings, namely that the mass ratio of active to inactive components is increased which implies an enhancement of specific energy. The previously discussed overall performance deterioration for cathodes with low CB content and CB:B $= 1$ is apparent in the energy-power scheme. Concerning electrodes with high CB content and CB:B > 1, our measurements suggest that NMC is superior for high specific energy applications. Furthermore the advantage of LMO for high specific power applications is visible as above 400 W/kg$_{comp}$ these cells achieve higher specific energies than ones with NMC. However, to evaluate the specific power maximum which can be realized with the parameter configurations containing LMO, additional investigations with higher C-rates are required. Ragone plots are often used to evaluate optimal parameter configurations for particular operation loads. Figure 7b shows the two best parameter configurations investigated in this study and additionally another configuration which may be promising at C-rates above the scope of this study. For high specific energy applications, the best investigated configuration is the 22% calendered NMC cathode with high CB content, CB:B > 1 and high ML. For applications where rather low specific power of $\leq$ 400 W/kg$_{comp}$ is acceptable this cathode delivers the highest values for specific energy of 170 Wh/kg$_{comp}$. At about

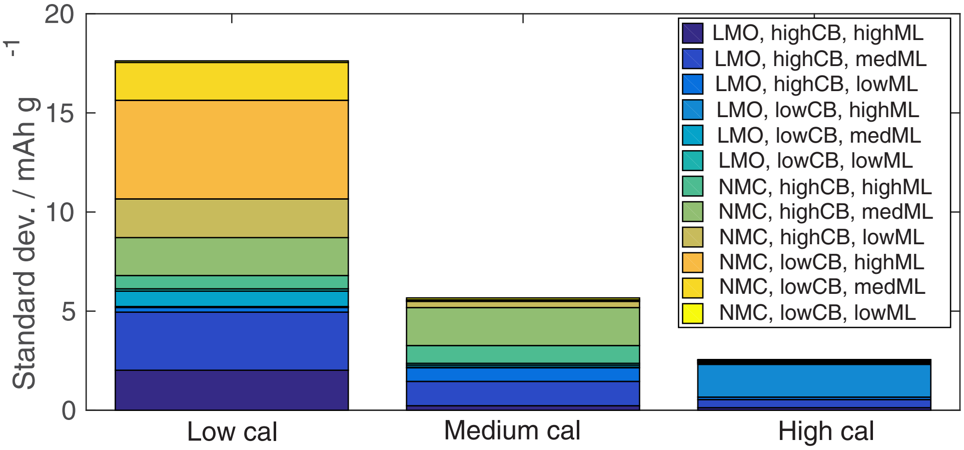

Figure 8. Impact of calendering level on accumulated standard deviations of discharge capacities at 0.2C for various cathode materials, carbon black contents and mass loadings.

600 W/kg$_{comp}$ the corresponding curve intersects with the one of the 30% calendered LMO cathode with high CB content, CB:B > 1 and medium ML. The latter is the best parameter configuration among the investigated samples for high specific power operations where more than 600 W/kg$_{comp}$ is required. This conclusion holds for C-rates $\leq$ 5C, the maximum measured in this study. As mentioned above, the evaluation of high specific power maximum of LMO with low ML is limited by the highest applied C-rate of 5C. A discharge current of 5C for cells with low ML is relatively small, compared to a discharge current of 5C for medium or high ML. This can be observed within the Ragone plot as the curve for LMO with low ML along the x-axis ends before a knee is reached or the specific energy approaches zero. For comparison: the curve of NMC with high ML reaches a knee at about 400 W/kg$_{comp}$, for higher specific power load the corresponding specific energy value decreases strongly. Further investigation with C-rates > 5C could show if the 30% calendered LMO cathode with high CB content, CB:B > 1 and low ML could deliver even higher specific power than the one with medium ML.

Correlation between statistical reproducibility and electrode design.—Among the four identically constructed cells per parameter configuration, significant standard deviations of discharge capacities occurred. These deviations increased with C-rate. It is assumed that at higher C-rates, more factors, especially kinetic processes are involved which contribute significantly to losses, e.g. electronic resistances and limitations of diffusivity and that this leads to an increase of performance inhomogeneities. Especially for the investigation of correlations between statistical scattering and production impacts it is interesting to observe that the extent of deviations varies between the investigated production parameters. This is shown in Figure 8. The strongest correlation was observed between extent of standard deviation of specific discharge capacity and the level of calendering. The depicted standard deviations refer to the measured discharge capacities at 0.2C and include the accumulated, i.e. the sum of the standard deviations of all manufacturing parameter configurations for the three calendering stress loads, respectively. Also, the contribution of each single configuration is visible. By far the highest standard deviations of discharge capacities were observed among cells with non calendered cathodes. The deviations decrease with the increase of calendering stress load. The largest improvement occurs between non calendering and the medium calendering level. It furthermore illustrates that calendering is not only an important step in the battery production to increase energy density and to improve aging properties but also to reduce deviations of product quality in terms of C-rate performance. We assume that the increase of performance deviations for low calendering stress loads is physically reasoned first by higher inhomogeneities within the particle-pore structure. E.g. the studies of Kang et al. and Antartis et al. show that pore radii[26] and porosities[27] among several electrode samples are more inhomogeneous for lower calendering configurations. Second, our previous investigations[3] and the work of Bockholt et al.[17] indicated that cathodes manufactured with too low calendering stress loads may suffer from partly disconnected electronically conductive pathways within the carbon black-binder matrix, similar to a loose contact in an electronical network which can be another reason for increased inhomogeneities of performance.

Conclusions

The impact of manufacturing parameters on battery performance of pouch cells was studied by producing and analyzing a large variety of cathode compositions. Graphite anodes with same composition and production parameters but different active material mass loadings were applied with NMC and LMO cathodes where various parameters were varied, being namely active material mass loading, calendering stress load and carbon black content together with carbon black to binder ratio. It was shown that among the investigated calendering stress loads, the highest calendering configurations yielded the highest discharge capacities, especially at higher C-rates. Low calendered and medium calendered cathodes showed poor performance in general. Additionally, the measured electronic resistances were enhanced so that it can be concluded that the performance losses arise mainly from poor electronic conductivity. Limits of ion transport which are expected to occur in electrodes which are calendered too strongly, appear to become only significant at calendering stress load beyond 22% for NMC and 30% for LMO. The investigations also revealed that specific energy could not be increased by reducing carbon black content to 4 mass-% and carbon black to binder ratio to CB:B = 1, at least not for applications where C-rates $\geq$ 0.2C are required, as due to the deterioration of electronic conductivity in the cathodes high performance losses emerged. Eventually by an optimized dispersion process the performance of smaller carbon black contents and CB:B ratio may be improved as discussed by Bockholt et al.[17] The comparison between the performances of NMC and LMO depict a characteristic advantage of NMC at lower C-rates below 2C which makes it attractive for high energy applications as in full electric and plug-in hybrid electric vehicles, whereas LMO performs superior at higher C-rates which is rather advantageous for high power applications as in hybrid electric vehicles. Also for fast charging applications, LMO may be an attractive alternative if other drawbacks as low cycling stability can be solved. The high C-rate capability of LMO is attributed to enhanced lithium diffusivity due to the three-dimensional spinel structure. The C-rate at which LMO becomes superior to NMC depends on the production parameters; it was shown that the C-rate above which LMO becomes superior to NMC can be shifted toward higher C-rates by increasing the calendering stress load. The parameter configuration of best performance for operation with the emphasize on high specific energy was achieved by 22% calendered NMC cathodes with high carbon black content, CB:B > 1 and high mass loading. For very high specific power applications, 30% calendered LMO cathodes with high carbon black content, CB:B > 1 and medium to low mass loadings showed the best performance. A statistical analysis revealed that calendering is of crucial influence, because it enhances the reproducibility of performance among cells for given parameter configurations. Therefore, in order to produce cells with constantly good performance it is recommended to apply sufficiently high calendering configurations. Overall the results only reflect the performance of pristine cells and do not take aging effects into consideration.

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