

Insights into Influencing Electrode Calendering on the Battery Performance

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As the demand for lithium-ion batteries (LIBs) continuously grows, the necessity to improve their efficiency/performance also grows. For this reason, optimization of the individual production steps is critical. Calendering is a crucial production step whereby electrode coatings are compacted to targeted densities. This process affects the porosity, adhesion, thickness, wettability, and charge transport properties of the electrodes, as well as the homogeneity of the coatings. Optimal calendered electrodes improve volumetric energy density, cyclic stability, and rate capability of the cells and also enhance the structural stability of the active material, which affects electrode safety and polarization. This article outlines the fundamental processes and mechanisms, as well as how modeling, simulation, and tomography can be used to optimize these processes. Additionally, the influence of calendering on a wide range of anode and cathode active materials is discussed. This review serves to give a deeper understanding into the calendering process-structure-performance relationships, and how they can be optimized to improve the performance of LIBs.

main concern for the LIBs since their inception in 1991. At the time they could achieve specific energy of 100 Wh kg^{-1} , for about $\$1000/\text{kWh}$, and currently up to 350 Wh kg^{-1} (800 Wh L^{-1}), for about $\$200/\text{kWh}$,^[1,2] with the outlook to further upgrade the specific energy to more than 400 Wh kg^{-1} (1100 Wh L^{-1}) for the near future.

In order to increase energy density, most research studies on LIBs have concentrated on various anode and cathode active materials, suitable binders and electrolytes, particularly for lithium-nickel-manganese cobalt-oxides (NMC) and silicon (Si)/carbon composite active materials.^[3,4] However, electrode and cell manufacturing development are also critical for enhancing the energy density, and other performance parameters such as cycling stability and rate capability of LIBs.^[5] Currently, the manufacturing

1. Introduction

In recent years, due to their high energy density the demand for rechargeable lithium-ion batteries (LIBs) has increased exponentially for recently emerging electric vehicles (EVs) and hybrid electric vehicles (HEVs), and it will continue to dominate the EV market, at least for the next 15 years. Despite their inherently high energy density, further improving the energy density has been the

of LIB electrodes^[1,6–14] involves slurry mixing, all the way to cell building and welding processes (Figure 1a). Calendering (Figure 1b) is a standard and low-cost (about 5% of the total cost)^[11] process in electrode manufacturing, which can increase the cell volumetric energy density and enhance the bonding strength between the active materials/conductive carbons/binders and the current collector by reducing the porosity from 50–70% down to 20–40%. Moreover, cells for different application like EVs and HEVs need different densities and, thus, calendering degrees. The impact of calendering parameters (line load, speed, and temperature) should be considered based on the material formulation, slurry solids content, and drying procedure. For instance, with increasing rolling temperature, the electrode's porosity and compaction resistance are decreased, and a higher adhesion strength is achieved.^[15] Higher line load during calendering could increase the energy density of cells, but the effective surface area and tortuosity for diffusion of Li-ions will decrease, resulting in an adverse impact on the power density of cells.^[16] Calendering to a certain level could improve the wettability of electrodes, due to the arrangement of particles and the increase in divergence within the pore networks.^[17] However, calendering beyond an ideal level reduces wettability, because of reduction in porosity and average pore diameter.^[18] Hence, the calendering process should be optimized to achieve electrodes with an overall optimum structure delivering sufficient electrical and ionic conductivities, adhesion and mechanical properties

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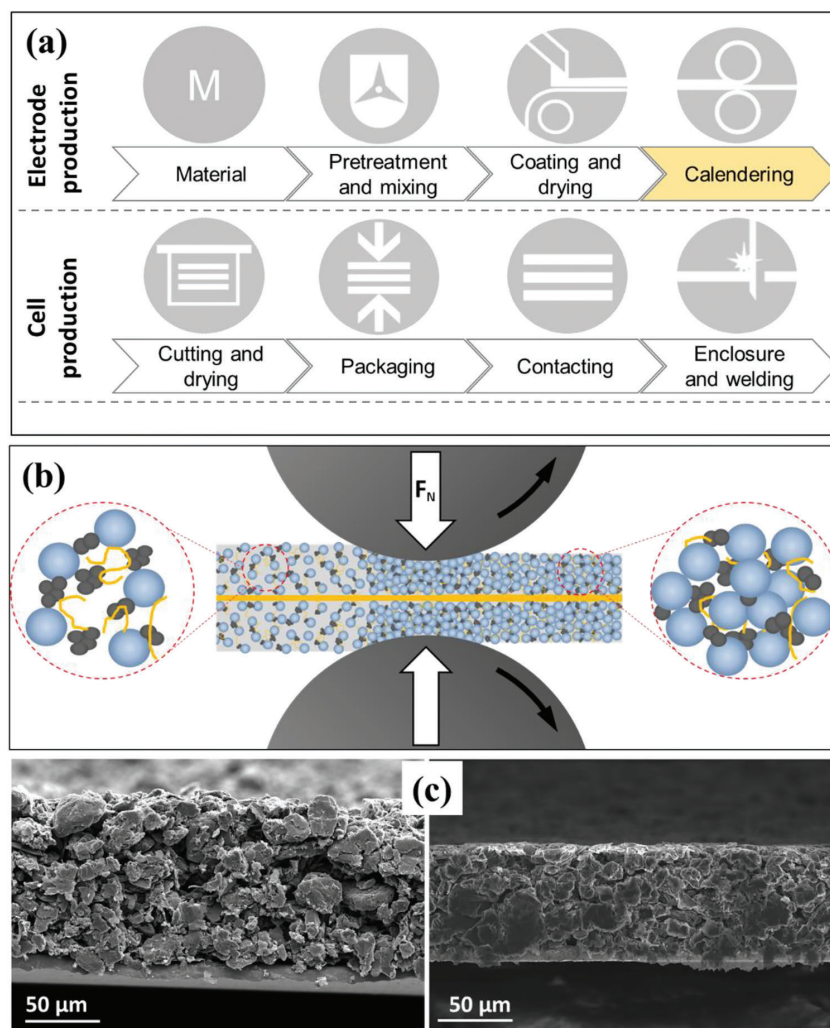


Figure 1. a) Schematic illustration of electrode production to cell production chain. b) Schematic illustration of the calendaring process and its effect on the electrode porosity and structure of a typical double-sided electrode. The blue and black particles are active materials and conductive carbons, respectively, and the yellow shapes represent the binder. c) SEM cross-sectional images of a typical single-layer anode electrode (composition: 90 wt% graphite (Gr) active material, 4 wt% conductive carbon, and 6 wt% binder), before (left) and after (right) calendaring. The electrodes manufactured and calendered at Battery LabFactory Braunschweig (BLB).

in order to deliver a battery with a maximum volumetric energy density and a longer cycle life.

This review aims to outline the fundamentals of the calendaring process, and demonstrate how this process could be a performance enhancing step in LIB fabrication. The following sections will start with the calendaring process and related mechanism. Afterward, discussions about the simulation, modeling and tomography studies are systematically reviewed based on the porous electrode theory and electrode structures. Finally, the influence of calendaring on the mechanical and electrochemical behaviour of LIBs and other battery electrodes are discussed.

2. Electrode Calendaring Process

Calendaring is one of the important process steps in the production chain of electrodes (Figure 1a) for LIBs, as it determines the final electrode microstructure. After mixing, coating, and drying, the porous coating undergoes mechanical compaction, reducing the coating porosity and improving the volumetric energy density by reducing the coating thickness (Figure 1b). Typical scanning electron microscope (SEM) images of electrodes before and after calendaring are demonstrated in Figure 1c. Aiming to improve the surface and bulk uniformity of the electrodes, the typical calendaring process consists of a two-roll compaction process

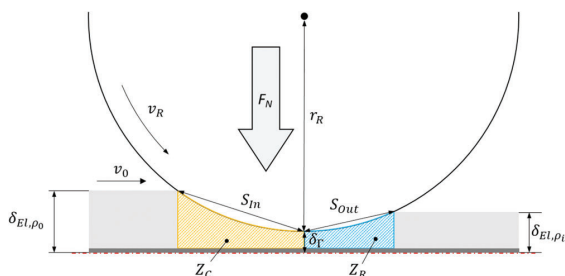


Figure 2. Schematic view of the in-gap circumstances, including the roll force F_N , the electrode thickness before (δ_{El,ρ_0}) and after (δ_{El,ρ_t}) the calendaring, the in-gap width (δ_Γ), the roll radius r_R , and the inlet and outlet strings S_{In} and S_{Out} . Z_C describes the compaction zone and Z_R the relaxation zone of the coating.

in which the electrode is drawn in the calender gap where the force, F_N , is applied. Typically, the force, F_N , is normalized by the coating width, w_C , and referred to the line load q_L (Equation (1)).

$$q_L = \frac{F_N}{w_C} \quad (1)$$

Within the roller gap particle rearrangement and, for high line loads, particle breakage occur,^[19] resulting in plastic deformation.

Additionally, an elastic deformation mainly of the active material occurs, leading to a fast elastic recovery (spring back) of the electrode directly after leaving the roller gap. Besides the line load, the gap width, δ_Γ , and the circumferential speed, v_0 , are the main control parameters (Figure 2).

The rolling radius, r_R , the electrode geometry (width: w_C and thickness: δ_{El,ρ_0}), and gap width, δ_Γ , define the electrode's catchment area within the gap through the contact area, A_Γ . The contact area and the calendaring speed define the dwell-time of the coating within the roller gap. According to Equations (3) and (4), the contact area depends on the roller radius, increasing the roller size leads to a larger contact area and a higher dwell-time. Higher dwell-time means more time for particle rearrangement, heat transfer, and a smoother compaction process with less shear stress. By ignoring the relatively small curvature within the roll gap, the contact area, A_Γ , can be calculated through the coating width w_C and the inlet and outlet strings S_{In} and S_{Out} (Equation (2)).

$$A_\Gamma = w_C \times (S_{In} + S_{Out}) \quad (2)$$

$$S_{In} = \sqrt{r_R \times (\delta_{El,\rho_0} - \delta_\Gamma)} \quad (3)$$

$$S_{Out} = \sqrt{r_R \times (\delta_{El,\rho_t} - \delta_\Gamma)} \quad (4)$$

The different deformation behavior of the current collector and the coating not only compression, but also strain perpendicular to the compression, and the occurring electrode spring back, may lead to different electrode defects,^[17] resulting in electrode

scrap and complicating ongoing process steps, such as cutting and packaging. Those electrode defects may be reduced by using a heated calendaring process. Heating the rolls reduces the needed line load,^[15] and a lower line load reduces the spring back of the electrode^[20] and the shear stress between the current collector and the coating. Overall, a well-designed and intelligent process control is necessary to reach desired product properties and quality.^[5]

2.1. State-Of-The-Art

The effect of the calendaring process differs between anodes and cathodes and depends on the used electrode chemistry. As the calendaring process affects the particle network as well as the pore network, it strongly influences the electrical, electrochemical, and mechanical properties of the electrodes. Regarding the mechanical characterization, Haselrieder et al. introduced a method based on nano-indentation and reported that the calendaring process mainly reduces the plastic deformation energy of the electrode while preserving the elastic deformation energy, which is important for the ongoing process step and the cycling capability.^[21,22] Furthermore, analysis methods based on nano-indentation or micro-manipulation^[22] can characterize the mechanical behavior of active material and correlate the results with the calendaring process.^[22–25] A good electrochemical performance is critical for battery cells in practical applications. The effect of calendaring differs significantly from anodes to cathodes, but also from the used material composition. On the anode side, a moderate compaction rate has been reported to be beneficial as it may reduce irreversible capacity loss while improving cyclability.^[21,22,26,27] Conversely, higher compaction rates were reported to reduce the cell performance due to increased diffusion resistivity.^[21,22,28,29] As the calendaring process lowers the porosity, it affects the wettability. For graphite anodes, comparable results have been shown for the effects of wettability on the cell performance, and moderate compaction improves the wettability due to a positive alignment of the graphite particles. In contrast, higher compaction has a poor wetting ability due to the progressive reduction in porosity and pore size distribution.^[18]

In contrast to anodes, cathode active materials (CAMs) typically show poor electrical conductivity. Therefore, for cathodes, calendaring has a significant effect on cell performance, as after calendaring the electrical conductivity of cathodes can be improved due to a denser particle arrangement and a better bonding between the conductive additive and the active material. Studies for the CAMs, such as lithium cobalt oxide (LCO), lithium iron phosphate (LFP), NMCs and lithium–nickel–cobalt–aluminum–oxides (NCAs) have shown that by calendaring the electrochemical performance is improved due to a reduction in the electrical resistance.^[30–33] However, ongoing reduction in porosity by calendaring results in an ionic limitation through the increase in tortuosity and diffusion resistance. Additionally, with increasing calendaring load, particles' cracks are more likely to happen. Hutter et al.^[19] investigated the relationship between the moisture uptake and the calendaring process observing a higher moisture uptake for higher calendaring loads, and addressed this to an increased surface area due to particle breakage.

Balancing electrical and ionic conductivity while identifying the ideal electrode porosity is the main challenge and goal of the calendaring process. From cell testing with varied C-rates, the literature shows that the strongest calendaring degree does not equate with the best electrochemical performance. Rather, a good balance between compaction and porosity, which is responsible for the lithium-ion transport via diffusion, is necessary to achieve the best electrochemical performance in terms of specific energy^[21] or for a percentage comparison between specific energy at different C-rates and initial specific energy.^[34] Regarding the long-term cycling of cells with calendared electrodes, it is much harder to separate the influence of the calendaring process step from other parameters, for example, material aging. Haselrieder et al.^[21] demonstrated the best cycle stability for the electrode with a compaction degree of 10%, whereas the electrodes with a compaction degree of 5% and 26% performed worst. Schilcher et al.^[35] investigated the long-term electrochemical performance of lithium manganese oxide (LiMn₂O₄, LMO) cathodes with six different coating densities (from 1.63 to 2.35 g cm⁻³). Here, the coating density of 1.82 g cm⁻³ showed the best long-time stability, and the two electrodes with the highest coating densities of 2.35 and 2.12 g cm⁻³ displayed accelerated cell aging, resulting in a faster decrease of accessible specific capacity.

The following sections take a closer look into the different interactions between the calendaring process and their influence on material-related properties.

2.2. Empirical Modeling

The first attempts to model the calendaring process step from empirical data were shown by Haselrieder.^[22] The line load was considered as a function of the compaction degree, Π , (Equation (5)), which itself is defined as 1 minus the ratio of the height of the electrode after the compaction process, $\delta_{E,a}$, to the height of the initial electrode thickness, $\delta_{E,initial}$.^[21]

$$\Pi = 1 - \frac{\delta_{E,a}}{\delta_{E,initial}} \quad (5)$$

It was shown that in the area of $0 \leq \Pi \leq 0.25$, a potential fit could be used to describe the correlation between line load and compaction degree. Further, Haselrieder showed that higher line loads are required to achieve same density when using electrodes consisting only of active material and binder, compared to three-component electrodes (active material, binder, conductive agent). This phenomenon can be explained with the binder's mainly elastic deformation behavior and, therefore, higher spring back of the electrode after passing the calendar roll gap. In addition, Haselrieder correlated the required line load for compaction with the resulting coating density for LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂ (NMC111)-cathodes and for spherical Gr (meso-carbon micro-beads, MCMB)-anodes. Haselrieder chose a potential fit for the description of the required line load, q_L , (Equation (6)) for increasing the coating density from initial density after the coating process, $\rho_{C,0}$, to the coating density after calendaring, $\rho_{C,i}$, whereby two form factors A and B are used^[22]

$$q_L = A \times (\rho_{C,i} - \rho_{C,0})^B \quad (6)$$

This approach turns out to be a quadratic correlation with $B = 2$, and simultaneously small values for A ($A < 1 \frac{\text{cm}^3 \text{N}}{\text{g mm}}$), which means, in general, that doubling the coating density requires a quadruple line load. Considering this, and according to Equation (6), the increase of the coating density is theoretically always possible using line loads going up to infinity. In a real compaction process of composite structure, this is not possible due to limiting side factors like raw material density and breakage strength of the particles.^[22]

An improved empirical modeling approach was developed by Meyer et al. in several publications.^[15,36,37] The authors predict coating density as a function of applied line load during calendaring, using double-sided NMC cathode and Gr anode electrodes. In their first publication,^[36] they varied the production speed of the calendar line used, resulting in an accurate correlation between coating density, ρ_C , and applied line load, q_L . By plotting coating density against line load, defining the initial coating density, $\rho_{C,0}$, of the electrode after the coating and drying process, as coating well as maximal density, $\rho_{C,max}$, at minimal calendar roll gap, they obtained an exponential fit (Equation (7)). Furthermore, they introduced an electrode-dependent compaction factor called compaction resistance, γ_C , which works as a damping factor in this model approach:

$$\rho_C = \rho_{C,max} - (\rho_{C,max} - \rho_{C,0}) \exp\left(-\frac{q_L}{\gamma_C}\right) \quad (7)$$

A considerable advantage of this exponential fit is the convergence of the coating density up to a maximum value defined by material specific properties, such as raw material density and porosity value in cubic close packing.

In a further publication, Meyer et al.^[37] investigated cathodes with different active materials and coating thickness variation of NMC111-cathodes. The authors aimed for a proportionality factor, p , between the initial coating density and the maximum coating density after compaction. They assumed that p would be similar to the ratio between a simple cubic packing (scp; 47.64%) and a cubic close packing (ccp; 25.95%), which would be 0.54. The results from electrode compaction show that p tends to be around a value of 0.4. The author explained this with the structural rearrangement effect, whereby the additives are forced between the active material particles and, therefore, fill space that the active material particles are not capable of occupying due to their larger size. This leads to a decreased porosity of the electrode coating. As mentioned in their previous publication,^[36] different active materials used can lead to a specific active material-dependent compaction factor when maintaining a constant mass loading of the electrodes under investigation. Furthermore, a linear correlation was shown between the compaction resistance of electrodes with constant active material and increasing mass loading. With these two findings, Meyer et al.^[37] replaced the compaction resistance factor, γ_C , with a combination of the mass loading, M_C , and a material specific mass dependency factor, μ . Using the correlation between initial and minimal coating density with the proportionality factor, and replacing the compaction resistance, Equation (6) was adapted by using the coating porosity, ϵ , instead of coating density, ρ , resulting in Equation (8):

$$\varepsilon_C = \varepsilon_{C,0} \left(p + (1-p) \exp \left(-\frac{q_L}{\mu M_C} \right) \right) \quad (8)$$

Hereby, it has to be considered that in addition to mass loading or electrode thickness, respectively, the thickness of the current collector, for both anode and cathode production, plays an important role regarding the correlation between achieved coating density and required line load. Just from the geometrical point of view, a thicker current collector would be equivalent to higher mass loadings with otherwise the same conditions.

Besides active material and mass loading, the temperature of the calender rolls plays a major role in the compaction behavior of electrode coatings, especially of cathodes, due to the thermoplastic deformation behavior of the commonly used binder polyvinylidene fluoride (PVDF).^[15,38] Due to this, Meyer et al.^[15] investigated the calendaring behavior of NMC111-cathodes with varied carbon black (CB) and binder contents at different roll temperatures. It was shown based on a comparison of electrodes with different mass loadings that the compaction resistance decreases with the rising temperature of the calender rolls. It was also shown that a linear relationship for the influence of the roll temperature between glass temperature and melting temperature of the thermoplastic binder can be assumed for the mass-dependent factor, μ . This led to a modification of the calculation of the compaction resistance, γ_C , from the specific mass dependency factor μ and the mass loading, M_C , by taking the theoretical mass dependent factor at a roll temperature of 0 °C, the roll temperature, T_R , and a recipe dependent temperature coefficient ξ (Equation (9)) into account.

$$\gamma_C = (\mu_{0^\circ\text{C}} - \xi \cdot T_R) \cdot M_C \quad (9)$$

Implementing Equation (9) into Equation (7) led to a fit from empirical modeling of the dependency between applied line load and coating density or, respectively, coating porosity that covers the influence of mass loading, roll temperature, and coating recipe.^[15]

$$\varepsilon_C = \varepsilon_{C,0} \times \left(p + (1-p) \exp \left(-\frac{q_L}{(\mu_{0^\circ\text{C}} - \xi \cdot T_R) \cdot M_C} \right) \right) \quad (10)$$

New active materials, such as Si or NMC811, have recently been employed to enhance the gravimetric and volumetric energy density of electrodes or cells. These new materials come along with material-specific influences on the production process, as shown by Meyer et al.^[36] for NMC111 and Gr, and by Meyer et al.^[37] for NCA and different NMC materials. According to these material dependencies, Scheffler et al.^[25] investigated the calendaring behavior of Gr-Si-blend anodes with varied Si content, increasing required line loads with increasing Si content to achieve the same coating density as a Gr reference electrode. In parallel, the compaction resistances using the modeling approach from Meyer et al.^[36] increases with higher Si mass fractions. It was shown that the correlation between compaction resistance and Si mass fraction, w_{Si} , can be described with Equation (11) with $\gamma_{C, w_{\text{Si}}=1} = 170.0 \pm 6.4 \text{ N mm}^{-1}$:

$$\gamma_C = \gamma_{C,G} + (\gamma_{C, w_{\text{Si}}=1} - \gamma_{C,G}) \cdot w_{\text{Si}}^{0.4} \quad (11)$$

The authors led this dependency of the compaction resistance back to the higher hardness and modulus of elasticity of Si, compared to the comparatively weak Gr particles. Furthermore, it was shown from micro manipulation measurement that the Si-rich electrodes tend to have higher deformation work at constant indentation depth, as well as a lower ratio of plastic to elastic deformation behavior, which supports the assumption of a Si-dependent increase of the compaction resistance.^[25]

The modeling of the calendaring behavior of electrodes for LIBs from experimental data has made steady progress over the last years. For future applications, the usage of new cell chemistries, or improved active material will simultaneously require further development of the modeling work, particularly regarding mechanical behavior of active materials. Furthermore, new inline measurement techniques are required, like the direct roll gap measurement system developed by Diener et al.^[20] which can be used for a stronger linkage of the interactions between machinery, process parameters, and product.

2.3. Electrode Defects

From the view of the production side, electrodes for LIBs are a multilayer product consisting of different materials with specific material properties and deformation behavior. Due to this, dissimilar elastic and plastic deformation of the electrode layers takes place. The compaction does not only occur in the vertical direction between the calender rolls, the electrode is also deformed lengthwise and crosswise according to the direction of the production line. Here, it is important to mention that the thickness of the current collector and its material stiffness playing a major role regarding the total amount of deformation. The behavior of the electrode's different layers (active material layer and current collector) leads to wrinkles (Figure 3a) at the edge of the electrode coating, as the copper or aluminum foil protruding from beneath the coating are not mechanically deformed in the same way as the coated area.^[39–41] When the current collector is thicker, its material properties have a higher influence on the overall compaction behavior of the electrode and, therefore, the importance of the current collector increases. It can be assumed that the wrinkles are relatively smaller for thicker current collectors with otherwise the same conditions. Those wrinkles can be mainly responsible for imprecise electrode cutting and, therefore, impede an accurate stacking process during cell assembly.^[40] Furthermore, the wrinkles resulting from the different material deformation behaviors from the same applied stress can lead to inner mechanical tension, leading to a corrugation of the electrode as depicted in Figure 3b. The corrugation of the whole electrode also influences the stacking and packing process in the cell assembly.^[17,34] For a non-symmetric electrode coating profile, this inner tension also leads to a lengthwise arc-like shape of the electrode (Figure 3c).^[41] The first attempt to quantify the corrugation of the electrode after compaction was made by Mayr et al.^[42] using two measurement systems within the calendaring system. For this, they implemented an inline measurement system for the electrode thickness (confocal sensors) and an inline measurement system for the electrode topography, crosswise to the direction of production (laser triangulation sensor). Using the data from the electrode topography, the authors were

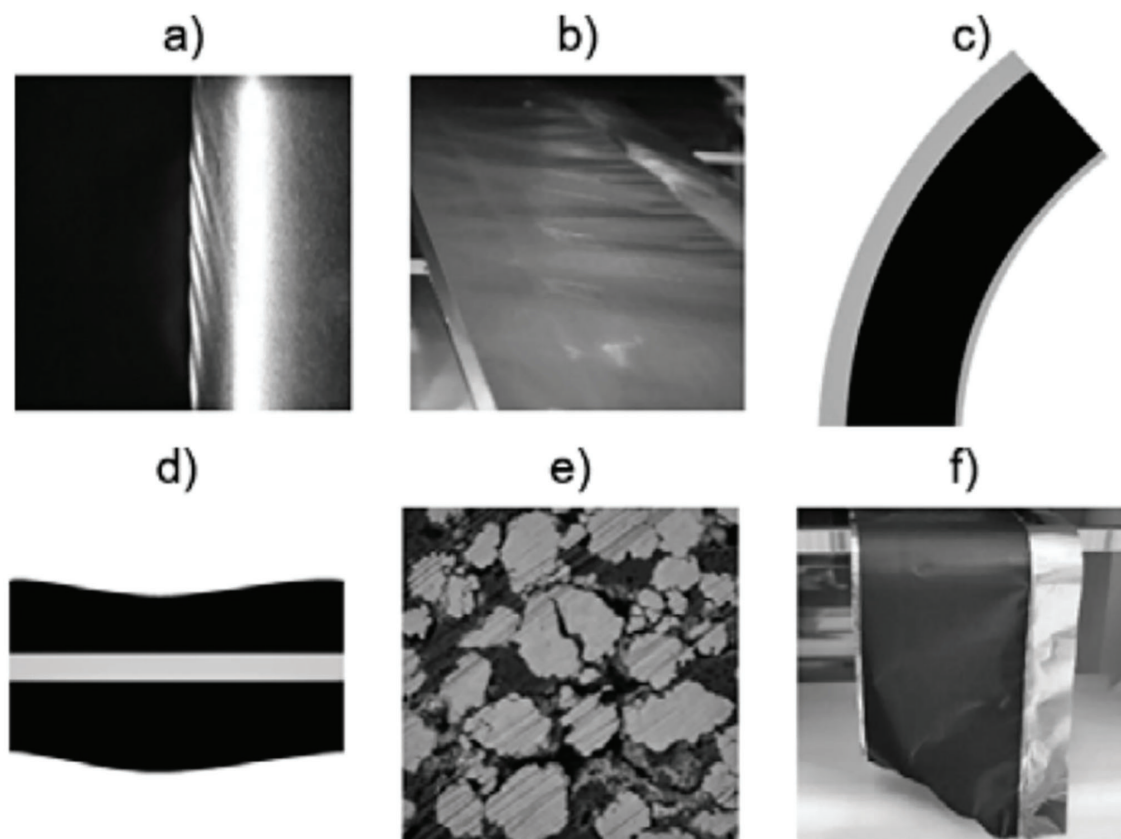


Figure 3. Electrode defects occurring from calendaring; a) wrinkles; b) electrode corrugation; c) arc-like electrode; d) inhomogeneous coating thickness; e) cracks of active material particles; f) electrode foil tear. Reproduced with permission.^[41] Copyright 2018, De Gruyter.

able to show an overall corrugation of the electrode itself with a peak-valley-value of $3.22\ \mu\text{m}$ and a corrugation of $1.36\ \mu\text{m}$ of the coating edge for an NMC cathode with a porosity of 30% after calendaring. Further development of inline sensor-based product control systems should cover an overall concept of the measurement of the electrode corrugation, the electrode thickness, and potential electrode defects. Combining these inline measurement devices with the modeling of the dependencies between process parameters and product properties, an agile closed-loop process control can enhance electrode quality, and decrease production scrap resulting from the calendaring process.^[42]

An unpredictable electrode defect that cannot be covered by using this inline measurement technology is an inhomogeneous coating thickness (Figure 3d), resulting from failure during the electrode coating process. Certainly, this electrode defect leads to an inhomogeneous stress distribution during compaction, which results in an inhomogeneous density of the electrode coating, leading to local capacity gradients of a battery cell.^[41] Applying normal and shear stress to the coating during calendaring forces the active material particle in the coating to collide. If the stress between the particles exceeds their breaking strength,

particles break as shown in Figure 3e.^[19,41] Huttner et al.^[19] investigated the calendaring behavior of NMC622 cathodes, focusing on particle breakages using BET surface measurement and moisture analysis of the electrodes. They found that with increased coating density, the moisture content rises linearly over the specific surface area of the electrode coatings in a range from 2.6 to $3.2\ \text{g cm}^{-3}$. Furthermore, they showed that the specific discharge capacity of the investigated electrode with a coating density of $3.2\ \text{g cm}^{-3}$ decreased, which lead back to the breakage of the active material particles, causing them to become more electrochemically inactive due to the breakage and lost contacts within the coating.

In general, if the internal stresses in the electrode coating, or between coating and foil, or the external stresses like tension in the direction of production, exceed the tear tension of the electrode itself, this forces electrode tearing (Figure 3f). The appearance of tears during production leads to production stop and production scrap. In all cases, electrode tears have to be prevented.^[41]

An overview of the impact on the further production process of a battery cell caused by the different possible electrode defects

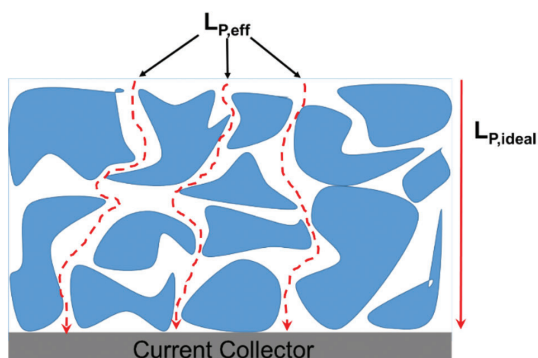


Figure 4. Schematic representation of the effective ($L_{p,eff}$) and ideal ($L_{p,ideal}$) pore length.

presented, was given by Günther et al.^[17] The authors divided the electrode defects into three classifications:

- Rejects, electrode useless for process
- May lead to rejection during the process
- Defect harmless for process

They declared that electrode corrugation is the most impactful electrode defect, mainly impacting the stacking and packaging process. Additionally, a tear of the electrode affects the laser cutting of the electrode to sheets, as well as the stacking and electrical contacting of the electrode sheets.^[17]

Overall, calendaring is a critical step during electrode manufacturing, and it can control the electrode film's adhesion, thickness, and porosity. It also controls the electrode tortuosity (τ), which is used to relate electrolyte conductivity and diffusivity due to the microstructure of the electrode.^[43] It is the ratio between the lithium-ion diffusion path through the coating and the coating thickness. In other words, it can be defined as the ratio between the effective pore length, $L_{p,eff}$, and the ideal pore length, $L_{p,ideal}$, using a cylinder as pore geometry (Equation (12)).^[44] the schematic representation is shown in **Figure 4**.

$$\tau = \frac{L_{p,eff}}{L_{p,ideal}} \quad (12)$$

As the electrode undergoes plastic deformation during calendaring, the pores and the pore structure experience a change, as already discussed. Froboese et al.^[44] introduced a method to determine the pore size distribution of electrodes based on mercury intrusion. Thus, they can also calculate an electrode's tortuosity based on porosity data. The authors investigated a Gr-based anode at five different coating densities between 0.84 and 1.58 g cm⁻³. The authors show a rising tortuosity with rising coating density for a compression rate up to 31%. The tortuosity decreases again for the strongest calendered electrode, with a compression rate of 47%. Simultaneously, the error bars from a double determination increase significantly, forcing the authors to assume strong destruction like particle detachment or particle cracks in the coating and, therefore, a non-homogenous electrode coating.^[44] Francois et al.^[45] investigated anode and cathode elec-

trodes via AC impedance and electrochemical impedance based on symmetrical cells, as shown by Landesfeind et al.^[46] For the cathode, the authors showed monotonically increasing tortuosity for porosity ranges between 0.52 and 0.29. However, the anode's tortuosity decreases at first when the coating is compacted from porosity of 0.55 to 0.43. The tortuosity undergoes a substantial increase afterward, when the electrode is further compacted to porosity of 0.41.^[45]

3. Modeling, Simulation, and Tomography

Experimental methods to investigate the influence of calendaring on the morphology and properties of electrodes can be costly in terms of raw materials, physical resources, and time. Moreover, a direct monitoring of the microstructure changes during calendaring is hardly or even not possible. Use of models and numerical simulation methods offer a far less expensive alternative. Modeling approaches can characterize everything from the mechanical behavior of individual particles^[47] to macro-scale models, focusing on global parameters in the electrode, such as particle distribution, porosity or tortuosity.^[24,45,48–53] Experimental approaches, such as X-ray computed tomography (CT) can be used to characterize the electrode microstructure and can be combined with models.^[54] Numerical models can help to better understand the complex factors that contribute to the electrode microstructure. This understanding is critical for optimizing the fabrication process, and to predict resulting performance of LIBs. Available software tools and modeling approaches are still somewhat limited, due to the non-linearity, and complexity of LIBs.^[55] However, much research has been done in recent years to improve the relevance of modeling approaches, which can be used toward improvement of LIB performances. In the following chapter, examples of modeling approaches will be given, demonstrating how these methods can be key to forming connections between the fabrication steps and battery performance.

3.1. Microstructure

Modeling of electrode microstructures can be used to predict compaction behavior depending on the electrode compositions. This was demonstrated by Meyer et al.,^[37] who used a Heckel-based model equation, supplemented by a predictive model, to predict the lowest achievable coating porosities after calendaring for different theoretical packing structures with varying particle size distributions and mechanical characteristics. Knowledge of the microstructure is also important for investigating tortuosity, a critical parameter for understanding Li-ion diffusion properties. Usseglio-Viretta et al.^[45] compared three different approaches for determination of the tortuosity factor (namely microstructure homogenization supplemented by mathematically complemented carbon binder domains, macro-homogeneous model fitting, and direct experimental measurements), and found that they were in good agreement for Gr and NMC electrodes. Forouzan et al.^[56] used shifted-force Lennard-Jones potential functions and granular Hertzian force to simulate particle interactions and evaluate the particle arrangement resulting from processing parameters. Lippke et al.^[57] modeled the structure formation during

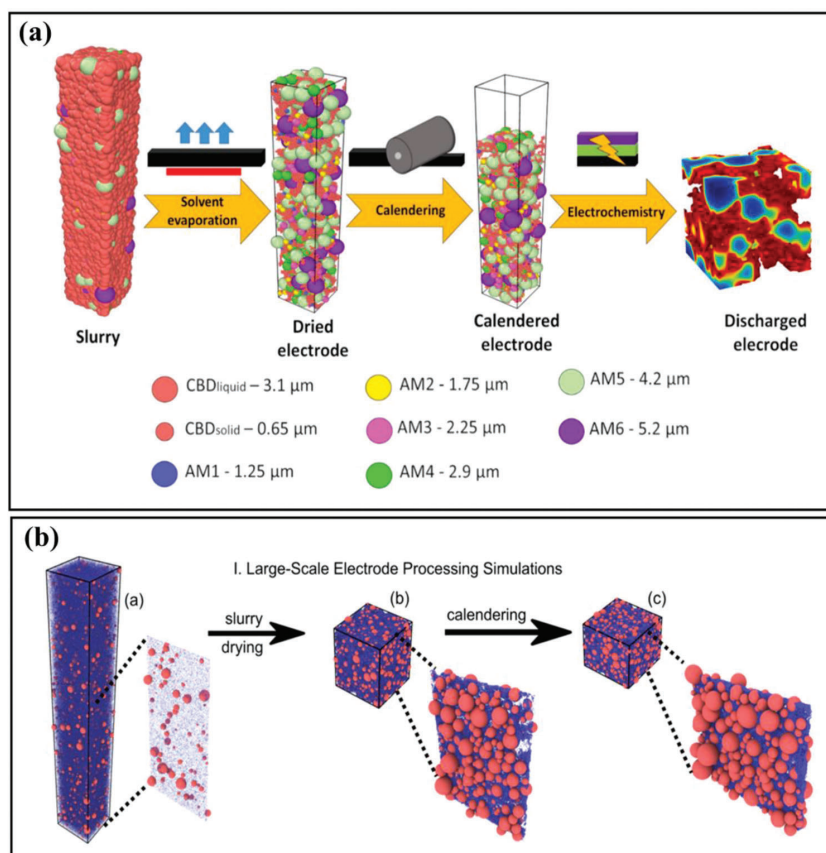


Figure 5. a) Demonstrates a computational workflow, starting with the slurry (coarsed grain molecular dynamics, CGMD, simulation), to the dried electrode (CGMD simulation), to the calendered electrode (discrete element method, DEM, simulation) and finally the assessment of the electrochemical performance (with continuum finite element method, FEM, models). Reproduced with permission.^[61] Copyright 2021, Elsevier. b) Demonstrates granular and colloidal dynamic simulations of the slurry, drying and calendering phase of electrodes, including cross-sections of the middle of electrodes. The AM particles are shown in red, the carbon-binder domain (CBD) phase in blue and the pore phase with the white region. Reproduced with permission.^[65] Copyright 2020, American Chemical Society. c) Demonstrates the workflow for generating a 3D computational finite element mesh from a combination of 3D image data and an analytical CBD “binder bridge” algorithm. Reproduced with permission.^[66] Copyright 2020, The American Society of Mechanical Engineers.

drying using the discrete element method (DEM) by using surrogate models for relevant fluid effects and could predict the coating porosity for different mass loadings. As most electrode microstructural simulations focus on spherical particles, Becker et al.^[58] Modeled the influence of particle shape on the mechanical compression and resulting transport properties of electrodes for non-spherical particles, using a novel random close packing algorithm.

As each process step can be highly dependent on one another, many microstructure investigations include simulations of multiple process steps. For example, Nikpour et al.^[59] proposed a multi-phase smoothed particle model, derived from smoothed particle hydrodynamics (SPH), to simulate the drying and calendering steps of electrode production. They found in previous manufacturing models that DEM can have unstable interfaces while trying to maintain liquid- and solid-type behavior, a dis-

advantage that can be compensated for by employing the SPH model in a DEM-style environment. They used a similar model in another study^[60] to investigate the effects of AM particle shape, size, orientation, and stiffness on the resulting microstructure after calendering. Ngandjong et al.^[61] also employed a DEM type model to investigate multiple processing steps, including slurry preparation, drying, calendering, and eventually, the electrochemical processes in the electrode, as demonstrated in Figure 5a. Lombardo et al.^[62] used a physics-based 3D model to mimic carbon-binder domain (CBD) migration during drying, and the impact of the drying process on the final microstructure after calendering. In a study by A. Shodiev et al.^[63] the calendering and electrolyte wetting steps were investigated with a 3D-resolved lattice Boltzmann method (LBM) to understand the influence of the electrolyte microstructure on the electrolyte wetting processes. Another study by Lombardo et al.,^[64] used 3D modeling to in-

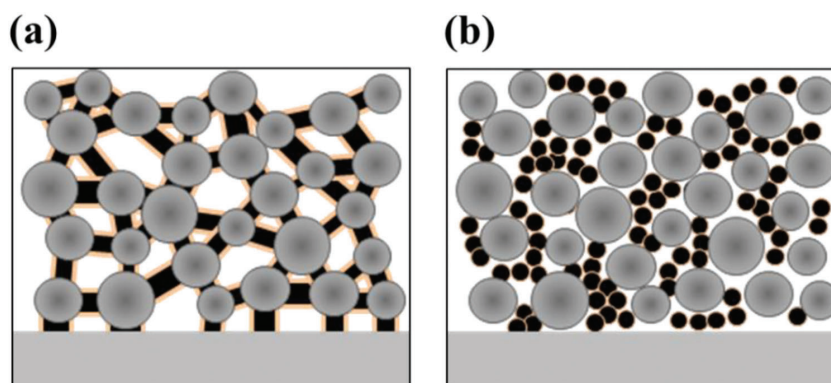


Figure 6. Schematic overview of both modeling approaches for the inactive material: a) Bond approach and b) carbon-binder domain (CBD) particle approach. Active material and current collector in gray, inactive material in its respective form in black.

investigate the dispersion, drying, and calendaring steps on the electrode microstructure, and their influence on electrochemical performance. In an investigation of the structure of the CBD and AM in the electrode, Srivastava et al.^[65] used the open-source molecular dynamics software LAMMPS to simulate the colloidal and granular dynamics, and investigate a strategy to engineer the electrode mesostructures through control of the CBD cohesion and the adhesion strength between the AM and CBD phases. Their approach is demonstrated in Figure 5b. This strategy was shown to have the potential to control transport properties in the electrode (including electronic and ionic conductivity and active material surface area availability).

Tomographic imaging can be an essential technique for investigating electrode microstructures. Westhoff et al.^[52] used 3D reconstructions from tomographic imaging of the microstructure of electrodes with different calendaring densities to investigate multi-layer cathodes and correlate the microstructure with the electronic resistivity. As the microstructure of the CBD can be difficult to resolve separate from the CAM, due to the differences in attenuation of these materials, Lu et al.^[53] employed a dual-scan superimposition X-ray CT technique to produce 3D reconstructions of both the NMC and the CBD to give a detailed overview of the microstructural inhomogeneities before and after calendaring, including the slurry phase. In a study by Trembacki et al.^[66] 3D reconstructions with X-ray CT, combined with a binder bridge algorithm (to estimate the mesostructure of the CBD), were used with finite element effective property simulations to analyze heterogeneity and trends (such as tortuosity and effective conductivity) across the electrodes, to determine the influence of calendaring on the performance. Alternative experimental techniques can be combined with modeling to understand the microstructure, as shown by Malifarge et al.^[67] who used X-ray diffraction to evaluate the proportion of oriented anisotropic particles in the electrode.

3.2. Mechanical Properties

Understanding the mechanical properties of electrodes can help to predict the influence of calendaring on the electrode. Often

investigation of mechanical properties goes hand-in-hand with microstructural investigations or other electrode properties (e.g., tortuosity, porosity, etc.). One of the most important applications for understanding the mechanical properties of the coating is to understand the mechanical stress induced in the coating in response to the calendaring process itself.

Different approaches exist for the mechanical simulations during the calendaring process, which mainly differ in the representation of the CBD (**Figure 6**): In some instances, the CBD was simulated by Sangros et al.^[24,68,69] and Ge et al.^[70] using solid-state bridges (bonds), while, for example, Ngandjong et al.^[61,62] used CBD adhesive surrogate particles. Both approaches were demonstrated to be capable of depicting the mechanical behavior of the electrode correctly. The solid-state bridge approach of Sangros et al.^[68] was also used for the modeling of heat conduction in electrodes in the context of calendaring by Lippke et al.^[71]

Sangrós Giménez et al.^[24] proposed a DEM approach to describe the mechanical properties of NMC cathodes with the elasto-plastic Thornton–Ning contact model, to model mechanical behavior of the NMC particles, and a dissipating bond model for the CBD, capturing the viscoelastic response of the electrodes during calendaring and quantifying the elastic recovery. The resulting porosity evolution for the calendared electrodes from their study is demonstrated in **Figure 7**. A study by Zhang et al.^[72] developed DEM simulations based on the Edinburgh elasto-plastic adhesion (EEPA) contact model to analyze electrode microstructure responses to calendaring. In addition, combinations of both approaches exist, as shown by both Schreiner et al.^[73] and Ge et al.^[70] who demonstrated that a combination of the EEPA and bonding contact models facilitated an effective description of electrode behavior. In multiple studies, Schreiner et al.^[73,74] also used DEM to investigate the influence of calendaring on the electrode parameters, such as compaction resistance, elastic spring back, and initial particle cohesion. DEM simulations were also used in another study by Sangrós Giménez et al.^[69] to gain information about the mechanical integrity of calendared electrodes and the development of mechanical stress within the structure due to lithiation, as well as estimate the adhesion strength of the electrode. Ge et al.^[70] carried out similar works to Sangros and compared the tortuosity of the virtual electrode with X-ray

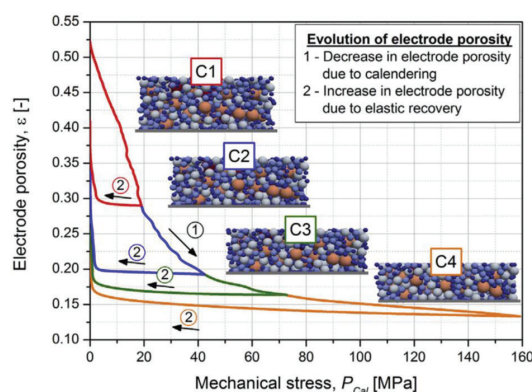


Figure 7. a) Demonstrates porosity evolution for electrodes subjected to calendaring processes. Reproduced with permission.^[24] Copyright 2019, Elsevier.

tomography data. Stershic et al.^[75] investigated the particle contact distribution within NMC electrodes using fabric tensors and compared DEM data with X-ray tomography,^[75] although their modeling approach had shortcomings, likely due to the inadequate consideration of the CBD.

These studies demonstrate that the complexity of a real-world electrode requires combinations of multiple approaches (both in modeling and with experimental techniques, such as X-ray tomography) in order to accurately describe the mechanical behavior of the electrode microstructure.

3.3. Electrochemical Properties

The link between microstructure and electrochemical performance is well-known, as properties such as porosity or tortuosity can have direct implications on charge transfer processes. This link is still perhaps not fully understood, and modeling processes offer a way to gain deeper insight into the connection between electrode microstructure, properties and electrochemical performance, especially in the case of electrodes subjected to the calendaring process, which alter the microstructure.

Simple electrode parameters, such as porosity, have been useful for predicting the electrochemical performance of electrodes. The porous electrode theory (PET) model, developed by Newman et al.^[76] has been shown by Smekenset et al.^[55] to reliably predict material and battery manufacturing parameters and for interpreting the performances of LIBs, based on given manufacturing parameters.

Investigation of capacity fading can also be supplemented with modeling approaches. Purewal et al.^[77] used a coupled chemical-mechanical degradation model to address calender loss and variable discharge rate and describe capacity fade over different operating conditions. The impact of calendaring on LIB performance was also investigated by Lenze et al.^[51] using pseudo-2D (P2D) model simulations. They demonstrated a correlation between capacity losses during cycling and the electrode morphology with calendaring parameters. For investigations of electron and ion transport in electrodes with different compression ratios, Laue et al.^[78] used a 3D micro-structural model to derive electrode

properties relations for the ionic and electric conductivity and applied them in the P2D framework of the Doyle–Newman electrode model, allowing them higher accuracy in predicting optimal porosities than with the classical P2D model.

The influence of calendaring on the electrochemical performance was also investigated by Lenze et al.^[79] using a P2D physico-chemical battery model, based on the work by Legrand et al.^[80] In a coupled multi-level model approach, Schmidt et al.^[81] and Thomitzek et al.^[82] combined a P2D model for simulating the battery cell, with a process chain model in order to analyze process–structure–property relationships and analyze the influence of tolerances in the manufacturing process on the processing parameters. They demonstrated that uncertainties in the calendaring performance produce broad porosity distributions and that mass loading and thickness deviations have the highest impact on cell performance. Ngandjong et al.^[61] were able to couple their calendaring simulation with preceding drying simulation and with electrochemical simulations were able to depict the influence of the calendaring degree on the electrochemical performance.

Nelson et al.^[47] used geometric characteristics of NMC particles subjected to calendaring or ball milling, extracted from X-ray nanotomography measurements, applied as computational domains in multi-physics transport models to investigate the Li concentration gradients within an NMC particle during the intercalation process. They found that the calendaring step significantly decreased the time needed for the intercalation process, and ball milling further reduced it. Modeling can also be used to investigate macroscale Li distribution, as demonstrated by Kespe and Nirschl et al.^[48] who mapped the spatial Li distribution within solid microstructures for different particle arrangements, demonstrating that Li accumulated in regions with higher specific surface areas. The Li distribution within electrodes subjected to calendaring at different charge states was investigated by Ngandjong^[61] using DEM models, coupled to a coarse-grained MD model and a 4D-resolved finite element method (FEM) model to predict the electrochemical performance. Also, Chouchane et al.^[83] investigated the influence of the spatial distribution of CBD within NMC electrodes using 3D modeling approach. They found that having the inactive material phase spread on the active material as film results in poorer performance than agglomerate-like morphology due to a loss in active surface area. Shodiev et al.^[84] showed the significant effect of heterogeneities in porosity in electrodes on the ionic impedance and tortuosity factors and consequently, the overall capacity. It became apparent that the optimal electrode structure requires a decreasing porosity from the separator side to the current collector side. In the study by Lu et al.^[53] they simulated the discharge of the reconstructed cathode (from X-ray CT) at various C-rates. This simulation is demonstrated in **Figure 8**.

The surface free energy of electrodes will influence the wettability, which can strongly influence the transport properties and resulting performance. The Owens–Wendt–Rabel–Kaelble (OWRK) model was adopted by Davoodabadi et al.^[85] to calculate the surface free energy (SFE) of electrodes subjected to calendaring, and processed using solvent- or water-based methods. They demonstrated that the SFE decreases with increasing degree of calendaring, corresponding to lower electrolyte wettability. The wettability was also investigated by Davoodabadi et al.^[86,87] to in-

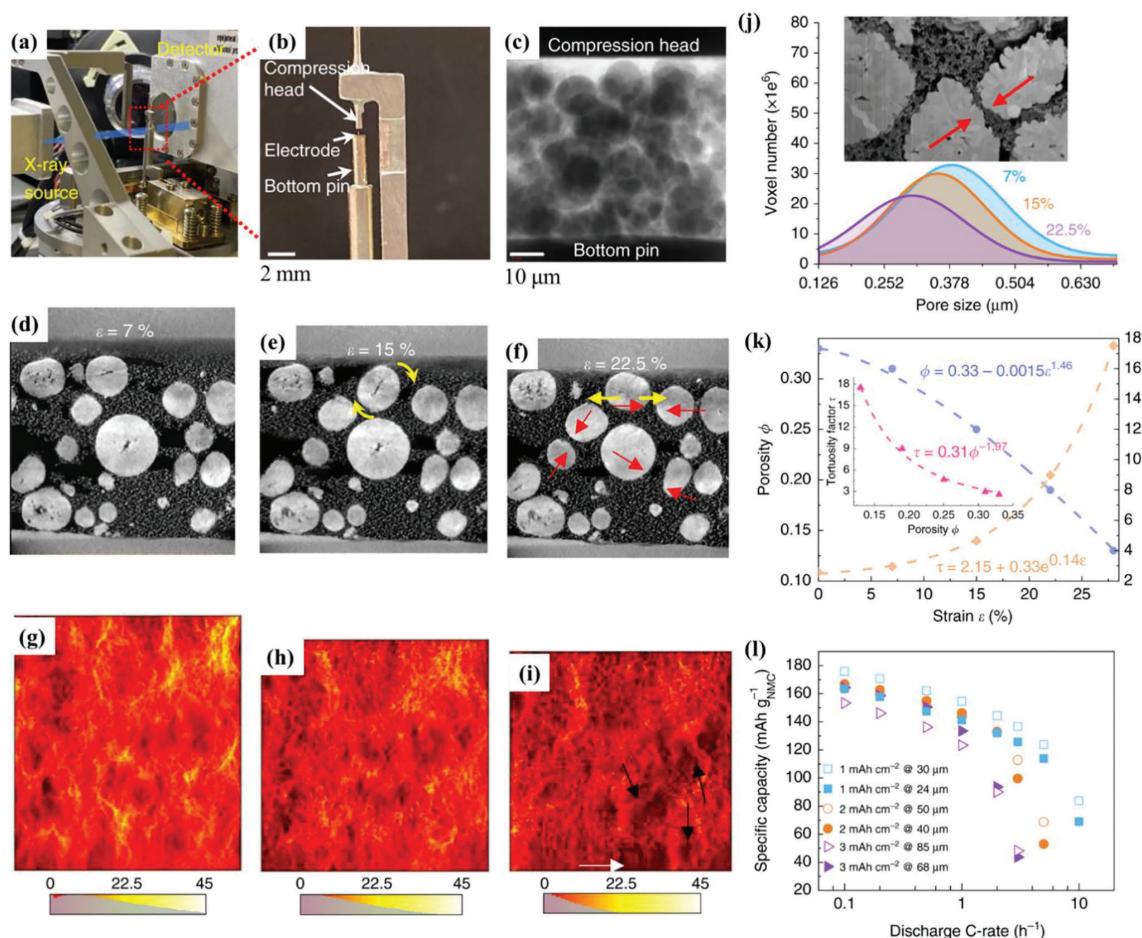


Figure 8. Calendaring effect on electrode microstructure and electrochemical performance obtained by X-ray nano-computed tomography and modeling. a) Experimental setup; b) photograph of the alignment; c) X-ray radiograph before the compression; d–f) images of the electrode microstructural evolution with different calendaring stages; g–i) graphical representation of the mass flux within the calendared pores structures; j) the pore size distribution associated with the calendaring steps; k) establishing the microstructural parameters according to the calendaring steps determined by the 3D reconstructions; l) A comparison of electrochemical performance between electrodes with three different mass loadings and whether they are calendared or uncalendared. Reproduced with permission.^[53] Copyright 2020, Springer Nature.

investigate the effect of the manufacturing parameters on wettability, by using calendared and uncalendared electrodes with several electrolytes, among other approaches. They assess the wettability using a solid permeability coefficient (SPC) for porosities between 30% and 55%, showing that the SPC value decreases for decreasing coating porosities. Thus, the wettability deteriorates with a more substantial calendaring degree as the pores size of the electrode shrinks, additionally to the overall decreasing free volume to take up the liquid electrolyte.

The studies discussed in this chapter have shown that modeling can be invaluable in planning of calendaring processes and predicting the results of cell performance. Application of modeling to process steps, especially calendaring, can serve not only to better understand the results, but also to predict mechanical and electrochemical properties of electrodes subjected to calendaring,

without having to undergo costly processing steps. Modeling approaches would also be invaluable for comprehending the influence of calendaring on the electrode microstructure and how it influences charge transport properties, especially at the critical electrode/electrolyte interface at the nanoscale. There is an intimate interplay between processing, electrode structure and performance, and the resulting mechanical properties, charge transport properties and electrochemical performance are thus closely related. Using modeling approaches can bring a deeper understanding of the relationship between these properties.

4. Performance of Calendared LIB Electrodes

Calendaring improves electrode adhesion and density, and increases the electrical conductivity between particles. Neverthe-

less, higher electrode density results in lower porosity, thus, obstructing electrolyte diffusion. Therefore, the electrode density and porosity should be optimized before using the cells.^[88] For instance, calendaring could reduce the electrode porosity from 60% to about 20% and 25% for Gr and NMC electrodes, respectively.^[36] Change in porosity and density of electrodes seriously affect the cell's electrochemical performance. In the following sections, the effect of calendaring on the mechanical and electrochemical performance of anode and cathode electrodes will be discussed.

4.1. Performance of Calendered Anodes

The AAMs play a critical role in LIBs, as these materials' physical and chemical properties directly affect the electrochemical performance of batteries. In addition to material choice, anode microstructure and, thus, density and porosity are essential to achieve a battery with high energy density and cycle life stability. The following sections will address the influence of calendaring on the mechanical and electrochemical properties of the most frequently used anode materials (e.g., Gr, Si, Si/carbon composites).

4.1.1. Graphite

Graphite (Gr) from synthetic or natural sources possesses a high degree of graphitization has been used as an AAM in commercial LIBs,^[89] owing to its favorable features such as low cost and relatively natural abundance, high electrical conductivity (1×10^5 (parallel to basal plane), 3×10^2 (orthogonal to basal plane)), exceptional cycle life, and theoretical capacity of 372 mAh g^{-1} . Besides many parameters such as the electrolyte conducting salt, type of Gr, binder, and conductive carbons, and their percentages, electrode microstructure also plays a key role in high-performance batteries. Electrode microstructure depends on the drying and calendaring processes, leading to a preferred orientation and internal pore structure.^[90,91] Additionally, the CB and Gr network becomes denser after calendaring, leading to higher electronic conductivity, owing to better contact points between the conductive additives and active material as they form a denser network after compression.^[92] As one of the first reported calendaring studies, Haselrieder et al.^[21] investigated different compression rates of 5–26% on the Gr electrodes. The electrodes with a compression rate of 10% delivered a good cycling life performance (200 cycles at 1C), even better than the uncalendered electrode. The calendaring of Gr electrodes at pressures of 0.1–0.3 tons cm^{-2} increases the reversible capacity and meaningfully enhances cyclability. The improved cyclability was attributed to better adhesion to the current collector.^[26] However, at higher compression rate (pressures about 4–8 tons cm^{-2}), calendaring of Gr electrodes has negative effects on the reversible capacity, and the first cycle Coulombic efficiency (CE), owing to the low ion diffusion within the liquid paths and also particle break-up at the highest compression rate.^[31,93]

Singh et al.^[12] manufactured thick (250–350 μm) single-sided Gr anodes and lithium–nickel manganese–cobalt–oxide (NMC) cathodes with different porosities obtained from the calendaring

process. They employed micron-sized carbon fibers to stabilize the thick electrode structure and to improve the electrode kinetics. The cell assembled with cathode and anode electrodes possessing porosities of 38% and 48%, respectively, showed a high energy density of 441 Wh L^{-1} at a rate of 0.1C, and better cycling stability with different C-rates. El Baradai et al.^[94] increased the reversible capacity from 85 to 315 mAh g^{-1} and electronic conductivity from 70 to 600 S m^{-1} , and reduced porosity from 70% to 34% by calendaring high porous bio-sourced printed electrodes. However, the specific capacity for the calendered electrode is significantly lower than the pristine electrode. Baunach et al.^[95] studied the influence of drying temperature on the internal electrode structure and demonstrated that adhesion force is strongly dependent on drying temperature: drying at higher temperatures decreases adhesion force. Subsequent calendaring improved adhesion, but ultimately did not eliminate the drying influence. Liu et al.^[96] developed a method for manufacturing Gr anode electrodes with a solvent-free technique to enhance adhesion strength through dry-spraying of PVDF, as an adhesion enhancer layer on the copper current collector, before Gr coating. The mechanical strength of electrodes and electrochemical performance (rate and cycling) are expressively enhanced using this fabrication method. In high energy density LIBs, lithium plating on the Gr anode surface under fast-charging conditions results in permanent loss of lithium from the cathode, instability of cathode structure, and thus capacity fading, which is the critical challenge that restricts fast-charging of LIBs.

Kazyak et al.^[97] made a conducting solid electrolyte ($\text{Li}_3\text{BO}_3\text{-Li}_2\text{CO}_3$) as an artificial solid electrolyte interphase (SEI) on calendered Gr electrodes (porosity of about 32%) using an atomic layer deposition technique. After the calendaring step, the deposition was conducted with a substrate temperature of 200°C (Figure 9a). This protective layer enabled an excellent cycle life with 4C charging (15 min) without lithium plating, and for the calendered electrode a capacity retention of 80% after 500 cycles in full-cell pouch cells, with an areal capacity of 3 mAh cm^{-2} , was achieved. Furthermore, CE was improved, and with a reduction in cell polarization, the energy efficiency of the charging process was enhanced. Klein et al.^[98] investigated a similar full-cell study with electrolyte optimization. They demonstrated that adding electrolyte additives strongly depends on the benchmark system's quality. In other words, the type of compression technique (calendered or hand-pressed Gr electrodes) before cell assembly could affect the benchmark system's electrochemical performance. Although both compression techniques exhibited similar electrode porosity (about 40%, and about 53% for an unpressed electrode) and similar visible surface appearance, the calendered electrodes performed better in the LIB full-cell. Dang et al.^[99] fabricated a low-tortuous Gr electrode, with high electrolyte infiltration, by a freeze-drying method. The calendaring does not affect the electrochemical behavior of the freeze-dried electrode except slightly decreased the CE of the first cycles from about 92% to 90.5%. However, this method for drying electrodes at the industry level is not economical.

Electrode production was investigated by Billot et al.,^[100] with a focus on the binder amount, the electrode thickness, and calendaring process, which are influential factors on the adhesion strength, a crucial parameter for the life span and the production of LIBs. They demonstrated that in the calendaring process,

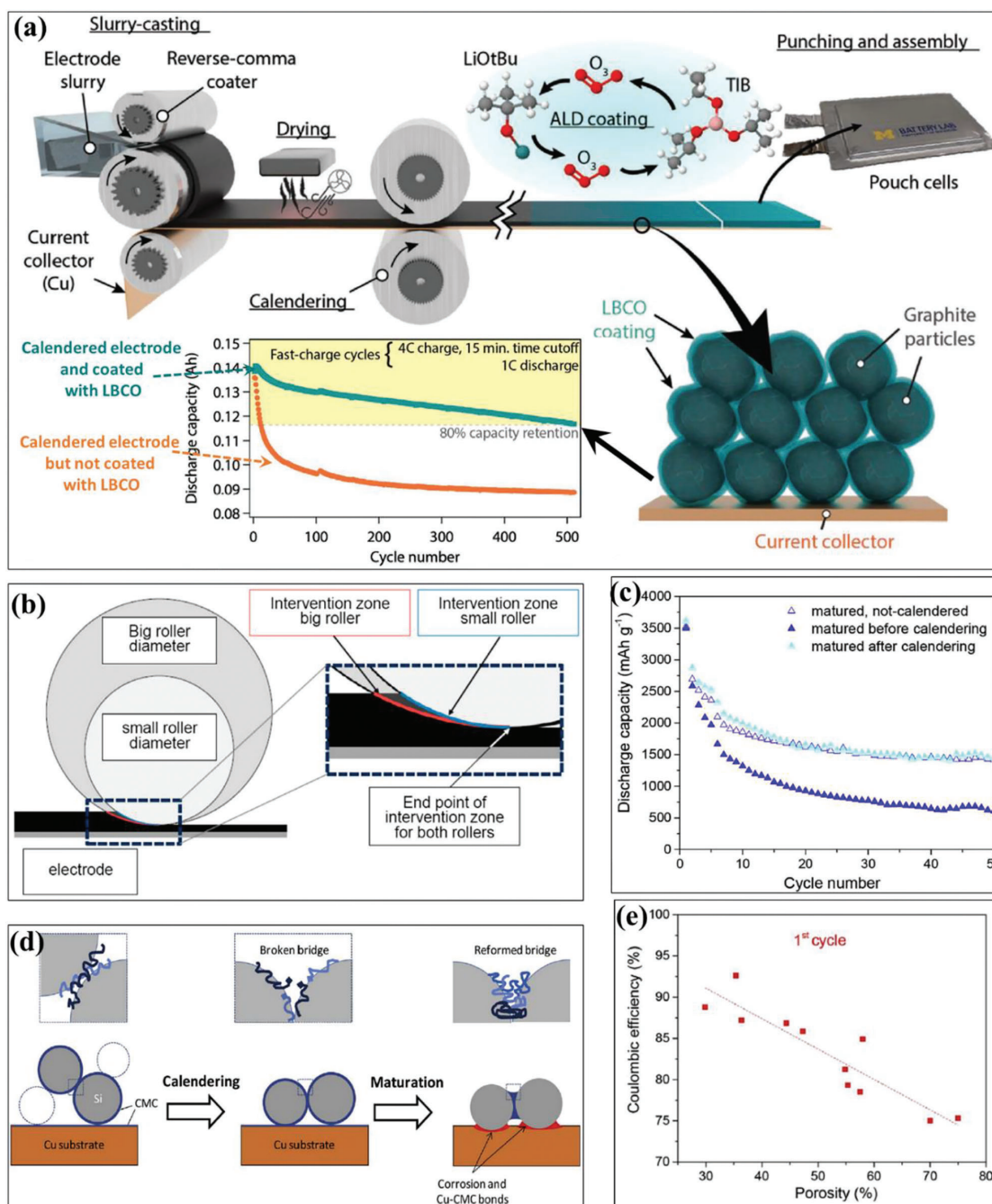


Figure 9. a) Schematic processes of the electrode fabrication, including coating a single-ion conducting solid electrolyte ($\text{Li}_3\text{BO}_3\text{-Li}_2\text{CO}_3$) via calendaring and atomic layer deposition for Gr electrodes. Also, discharge capacity cycling of NMC532/Gr pouch cells with and without $\text{Li}_3\text{BO}_3\text{-Li}_2\text{CO}_3$ coating at 4C fast-charge cycles. Reproduced with permission.^[97] Copyright 2022, John Wiley & Sons. b) Schematic representation of the thickness changes and the shear forces generated depending on the roll diameter. The larger roll diameters lead to higher adhesion. Reproduced with permission.^[100] Copyright 2020, John Wiley & Sons. c) Cycling performance of fabricated Si-based electrodes before or after calendaring (1 ton cm⁻²) at 480 mA g⁻¹, with a Si mass loading of about 3 mg cm⁻². d) Schematic illustration of the breaking-restoring of the particle/binder bonds after the calendaring-maturation processes. e) The effects of the electrode porosity on the first coulombic efficiency of Si-based anodes. Reproduced with permission.^[112] Copyright 2017, Elsevier.

with a decrease in the shear stresses by increasing the roll diameter from 200 and 400 mm, the adhesive strength is affected positively, and significantly increased it by 19%. The shear stress is decreased by increasing the roll diameter, because of the layer thickness reduction in the longitudinal direction (Figure 9b). Overall, larger roll diameters lead to higher adhesion strengths.^[35] Jang et al.^[101] used heat treatment on the fabricated Gr electrode, made with a pore-formation agent, polytetrafluoroethylene (PTFE). After the heat treatment, the PTFE particles were depolymerized to form micro-sized pores. The porosity of the electrodes was fixed to 30%, from about 50%, by calendering. The electrodes showed improved wetting ability, ionic diffusion rate, tortuosity, and electrode surface area, and ionic resistance and ionic polarization in the electrode were decreased. The fabricated electrode displayed a specific capacity of about 200 mAh g⁻¹, whereas a typical electrode only showed 140 mAh g⁻¹ at a high current density of 3C. The drawback of this work, compared to a standard Gr electrode, could be low electrode density and poor cycling life, because of the use of 40 wt% PTFE in the electrode, which is not pointed out in the paper.

Recently, our group^[102] developed a novel electrode production process (twin-screw extrude with the integration of manufacturing steps of coating, drying, and calendering into one continuous line), which is based on Gr anodes with a solid mass content of more than 50 wt%. This advanced electrode processing was enabled by selecting new binder materials, machinery design, and process parameters. Due to the binder being exposed to high mechanical/shear stresses within the twin-screw extruder (with a short-time for mixing) and calender gap, the binder type is a crucial parameter for a high-performance electrode. By applying this low solvent process design, the Gr electrodes with a density of about 1.3 g cm⁻³ were achieved, which is higher than the reference electrode made with the wet-coating method after drying (1.0 g cm⁻³); thus, a following calendering step after drying may not require for the twin-screw extrude with corrected calendering of wet electrode process.

4.1.2. Silicon

Si anodes, with ten times the theoretical capacity of graphite anodes, have attracted considerable research attention for next-generation LIBs comparing the specific capacity of 4212 mAh g⁻¹ for Li₄Si to Gr anode with only 372 mAh g⁻¹.^[103] Besides, Si is the second-most abundant element in the earth's crust, and it is environmentally benign and has low electrochemical potential. However, Si has a huge volume change during (de)lithiation, a common drawback in Si-alloy anodes, leading to severe particle pulverization and the formation of unstable solid-electrolyte interphase, leading to increasing internal resistance and rapid capacity decay.^[104–106] Many nano-engineering approaches effectively solve several problems related to the volume expansion of Si anodes.^[107,108] However, the practical application of these fancy anodes is challenging due to limitations such as low mass loading and calendering incompatibility, which can result even in a lower volumetric energy density than state-of-the-art Gr anodes. Specifically, during calendering, the structure of the anode can easily collapse under high pressure, damaging the porous features. Certainly, Si is usually a hard and brittle material, and thus

can have difficulties to withstand calendaring processes,^[109] but this is not the case for nano Si. The Obrovac group^[110] prepared a bulk quantity of layered amorphous Si powder by a chemical delithiation technique. Layered Si powders obtained from this method have large amounts of open volume between the Si layers that can accommodate volume changes during (de)lithiation. Compared to the bulk crystalline Si, the cycled layered amorphous Si electrodes exhibited a lower volume expansion during lithiation and enhanced cycling stability. The layered amorphous Si structure may become damaged during the calendaring process. However, the calendered electrodes showed similar cycling stability but higher volumetric energy density than the uncalendered electrodes. Yuca and Çolak^[111] studied the neutralization of polyacrylic acid (PAA) by NaOH, as a binder, and subsequent calendering process during Si electrode fabrication. The electrode loading was 1 mg cm². The first cycle CE increased from about 70 to 75% after neutralization and calendering, and also the cycling life stability after 100 cycles was enhanced for calendered electrodes from 862 to 1370 mAh g⁻¹. Karkar et al.^[112] manufactured Si (46 wt%) electrodes with an extra maturation step^[113] in an atmosphere with high humidity of about 80% R.H for 2–3 days after calendering and before post-drying and cell assembly. This maturation makes an important change in the electrode structure and improves the interface connection of active materials/conductive carbons/binder together with the current collector (Figure 9c–e), therefore, enhancing its mechanical strength with better electrochemical behavior.^[113] Applying the maturation step after calendering has a major advantage that restores the particle-binder cohesive bridges and makes a robust calendered electrode even with high active mass loading (3 mg_{Si} cm⁻²) and low porosity (30%). The electrode exhibited a capacity of about 1800 mAh g⁻¹ (5.4 mAh cm⁻²) after 50 cycles, with an improved CE. With decreasing porosity, the capacity retention and initial CE were increased. The CE increased from 75% to about 90% for the electrodes with porosities of 75% and 30%, respectively (Figure 8e). An improved electrochemical result for matured calendered Si/carbon electrodes were also obtained by Vanpeene et al.^[114]

Wang et al.^[115] prepared a Si structure with high stability at a pressure of over 100 MPa (the mechanical stress during calendering could be up to 80 MPa)^[35,93] by depositing a dense Si shell (using a Si layer of about 200 nm) onto each Si particle cluster. The fabricated particles meaningfully advance mechanical stability, and the structure of these particles remained undamaged after the calendering process (Figure 10a₁–a₄). The calendered electrodes demonstrated a high initial CE of about 90% and a high volumetric capacity of more than 2000 mAh cm⁻³. The excellent electrochemical performance can be attributed to the porous inner structure providing void space to accommodate the volume expansion during the cycling with an excellent calendering capability of the Si particles

The significant volume change of Si anodes could be relatively accommodated by common and costly methods to fabricate Si nanostructures and Si/carbon composites with void spaces in the particle structure. Thus, a low tap density and large surface area result in lower energy density and CE upon cycling, because of increased SEI formation reactions. To solve this issue, Lee et al.^[116] developed a milling method for producing micron-sized Si secondary particles with a high tap density (0.81 g cm⁻³) and a low surface area. The fabricated electrodes

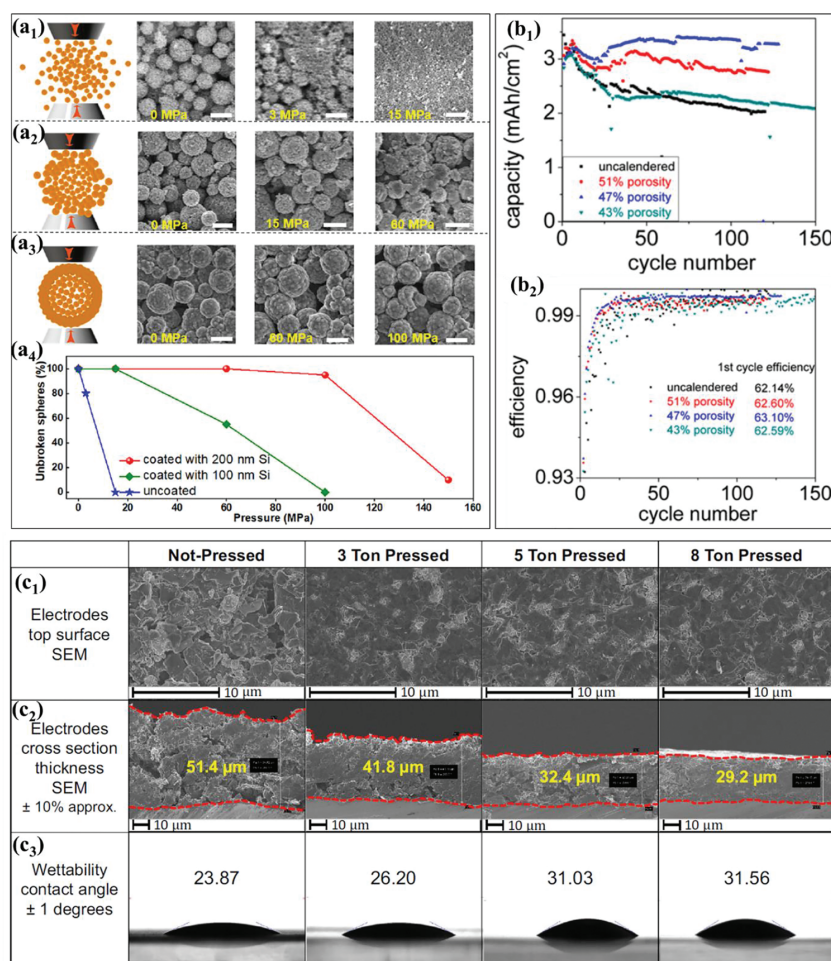


Figure 10. Pressure-resistant property test and SEM images (Scale bar is 2 μm) taken after calendaring on a₁) uncoated, a₂) 100 nm Si coating, and a₃) 200 nm Si coating on the Si nanoparticles cluster. a₃) The fraction of unbroken spheres after different calendaring pressures. Reproduced with permission.^[115] Copyright 2018, American Chemical Society. b₁, b₂) Cycling performance and CE of the SiO/ poly(9,9-dioctylfluorene-co-fluorenone-co-methyl benzoic ester) electrode after calendaring with different porosities at 100 mA g⁻¹. Electrode: 90% SiO and 10% poly(9,9-dioctylfluorene-co-fluorenone-co-methyl benzoic ester) binder. Electrolyte: 1.2 M LiPF₆ in ethylene carbonate/diethyl carbonate (3/7 w/w) with 30 wt% fluoroethylene carbonate (FEC). Reproduced with permission.^[118] Copyright 2015, American Chemical Society. c₁–c₃) Top surface and cross-sectional SEM images of Si-iron-manganese alloy electrode and electrode/electrolyte wettability results after different pressing pressures. Reproduced with permission.^[119] Copyright 2017, Springer Nature.

showed a density of 1.4 g cm³ after calendaring, and exhibited a volumetric capacity of 598 mAh cm⁻³ and excellent cycling stability, maintaining more than 95% of the initial capacity after 500 cycles, with a high CE of 99.7%. Wang et al.^[117] investigated Young's modulus (E) and hardness (H) of Si/PVDF composite electrodes at various state of charges (SOCs) and cycle numbers using nano-indentation for the both (un)calendered electrodes. The calendered electrodes have lower porosity (about 50%), thus for every SOC they have larger E and H values than the uncalendered electrodes (about 70%). Their data displayed that mechanical integrity is vital to advancing the electrochemical performance of calendered electrodes.

Zhao et al.^[118] optimized the porosity and density of SiO (with about 10% carbon coating)/ polymer composite electrodes using a calendaring process. The electrodes were calendered from a porosity of 63% to 43%. The calendered electrode with a density 1.19 g cm³ (porosity of 47%) enhanced cycling performance and energy density compared to the uncalendered and the other calendered electrodes. The calendered electrodes achieved an areal capacity of ≈ 3.5 mAh cm² at a 0.1C rate, which was an improvement of about 1 mAh cm² compared to the uncalendered electrode. CE, a critical value for long-term cycling, was improved from 99.33% to 99.76% for the electrode with 47% porosity; results are shown in Figure 10b₁, b₂.

Alaboina et al.^[119] fabricated a calendered anode electrode, Si–Iron–Manganese (Si–Fe–Mn, 80–18–2 wt%) alloy + Gr composite. The calendered electrodes were discussed in terms of porosity, electrolyte wettability, and long-term cycling (Figure 10c₁–c₃). Both specific capacity and CE are reduced by increasing of the calendaring stress, due to reduction in the core active pores of the electrodes. Cao et al.^[120] used the mechanofusion process to synthesize Si-alloy/Gr anode composite materials. The calendered electrodes resulted in an energy density improvement of about 10% with specific capacity of about 950 mAh g^{−1} at 1C during 50 cycles. Du et al.^[109] demonstrated that the energy density and cycling performance of Si-alloy electrodes could be enhanced if the alloy is combined with Gr and calendered to a porosity of about 20%. The calendered electrodes prepared with mixed Si/Gr using PVDF as a binder demonstrated a better cycle life, due to the stronger mass loading film.^[121] However, calendaring of Si-based anode electrodes prepared with non-PVDF binders (carboxymethyl cellulose / styrene-butadiene rubber (CMC/SBR), alginate, polyimide) considerably reduces their cycling stability, mainly because of the low porosity in the electrode after calendaring.^[122–124]

4.1.3. Si/Carbon Composites

In order to solve the above mentioned challenges of Si anodes for practical applications, many efforts have been carried out to achieve first high CE, a stable SEI, long-term cycle life and, of course, high volumetric energy density. For instance, fabricating Si/carbon composites with different techniques to obtain a variety of morphologies and structures, with unique material and electrochemical performance, have been frequently reported.^[3,125,126] Electrode calendaring, which can improve the volumetric energy density of batteries, is a vital process for preparing high-quality electrodes for practical applications. Regarding calendaring studies, Kierzek et al.^[127] synthesized a Si/carbon composite that consisted of Si and Gr micro-particles embedded in a pitch coke matrix via a heat treatment at 1100 °C. Besides the calendaring study, the effects of PVDF and CMC as binders for the preparation of the electrodes were investigated. Calendaring the electrode mass up to 30% of the initial film thickness was possible without electrode damage (for electrodes with a gravimetric capacity of about 500 mAh g^{−1}). However, a volumetric capacity of 670 mAh cm^{−3} was calculated for the calendered electrode, which is higher than the commercial Gr-based anodes (about 450 mAh cm^{−3}).^[128] Calendaring was performed to 100% (uncalendered), 60%, 40%, and 30% of the initial film thickness, which shows no effect on the cycling performance of anodes containing 12% Si in the composite. All anodes showed similar and very high CE. Therefore, calendaring improved the packing density to 1.35 g cm^{−3} without reducing the specific capacity, but increased the volumetric energy density.

Li et al.^[129] synthesized a porous Si/carbon composite, using an electrochemical etching technique, with pores of up to 50 nm in diameter. They showed that after calendaring some large porous Si/carbon particles were broken, but the structural integrity of particles remained unchanged. The calendered electrode exhibited a good electrochemical cycling performance with

an areal capacity of about 2.5 mAh cm^{−2} and a specific capacity of about 680 mAh g^{−1}, which was around 85% of the value for uncalendered electrodes. However, the cycling stability was similar to the uncalendered electrodes, with 90% capacity retention after 200 cycles.

Fei et al.^[130] developed a method to coating reduced graphene oxide (RGO)/ SiO micro-particles of 3–10 μm on the current collector without using any binder or conductive carbon. The uncalendered SiO/RGO electrode layers were loosely packed. However, the electrode layers became much denser after calendaring, and the electrode thickness was reduced to half of the uncalendered electrode. The calendered electrodes showed a specific capacity of about 1000 mAh g^{−1} over 100 cycles, with a first CE at about 70%. Li et al.^[131] manufactured the spherical granules of SiO_x/Gr/carbon composites using a spray drying process. The obtained granule particles possessed enhanced electrical conductivity (518 S m^{−1}) and maintained structural integrity during calendaring and following (de)lithiation processes. The calendered electrode anodes with a density of about 1.4 g cm^{−3} showed a better initial CE (83%) and a low volume expansion of about 14%, good cycling stability, and outstanding rate capability (about 90% of the original charge capacity remained at 5C). Nevertheless, the capacity retention of calendered anodes without a pitch coating is much lower than that of the uncalendered electrode anode with a pitch coating. Hence, the carbon derived from the pitch is critical in the Si/Gr composite anodes of LIBs.^[132–134]

Fabrication of porous structures is a well-known approach to overcoming the pulverization of Si-based anodes. Nevertheless, low mass loading and the poor mechanical strength (calendaring incompatibility) of these porous particles are challenging for high volumetric energy density batteries. Additionally, the uncalendered porous electrodes need more electrolytes, hence lowering the cell energy density. However, some studies^[104–107] developed unique approaches to fabricate high-performance calender-compatible porous Si structures as anodes of LIBs. Son et al.^[135] prepared a macro-porous design for a carbon coated Si/Gr composite anode (Figure 11), consisting of an ultrathin Si layer. This robust macroporous matrix can resist high pressure and preserve its porous architecture during electrode calendaring. The calendered composite electrodes, with a density of 1.6 g cm^{−3} and the active material content of more than 95 wt%, displayed an areal capacity of over 3.6 mAh cm^{−2} (and reversible capacity of 665 mAh g^{−1}) with an excellent first CE of about 91%, and a lower electrode swelling of 40%. Additionally, the calendered electrodes showed stable cycle life and retained a high energy density of about 930 Wh L^{−1} over 100 cycles, with mitigated electrode expansion (Figure 10b). Recently, Müller et al.^[136] investigated the effect of carbon coating and calendaring on Si/Gr composite particles produced in pilot scales of about 1 kg, which were manufactured via scalable fluidized bed granulation.^[132] The carbon coating improved the stability of composite particles and their electrical conductivity. The carbon-coated and uncoated electrodes were calendered to densities of approximately 1.0–1.45 g cm^{−3} (the density for uncalendered electrodes was about 0.8 g cm^{−3}). The calendered carbon-coated Si/Gr composites, even for the highest density (1.45 g cm^{−3}), showed a superior electrochemical performance. However, Si nanoparticles were detached during calendaring for the non-carbon coated composites, resulting in a quicker degradation at higher electrode densities. Therefore, af-

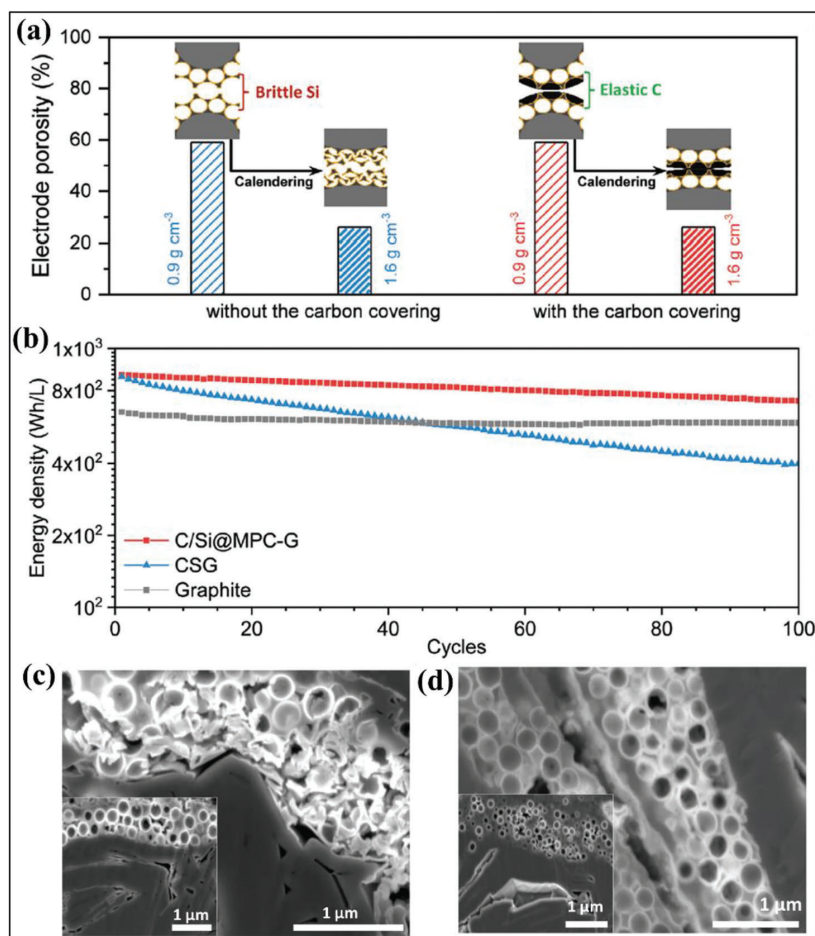


Figure 11. a) Effect of carbon coating on the calendaring capability of the porous structure of Si-coated macroporous carbon/Gr composites. b) Volumetric energy densities of electrodes for full-cell cycling. Cross-sectional SEM images of the electrodes after calendaring for c) Si coated macroporous carbon/Gr composites (Si@MPC-G), inset before calendaring, d) about 5 wt% carbon coated on Si@MPC-G (C/Si@MPC-G), insets before calendaring. All electrodes: active material/CB/CMC/SBR: 95/1/2/2. The areal capacities are 3.6 mAh cm^{-2} . Electrolyte: 1.3 M LiPF_6 in ethylene carbonate/diethyl carbonate (3/7 v/v) with 10% fluoroethylene carbonate (FEC). Reproduced with permission.^[135] Copyright 2020, John Wiley & Sons.

ter calendaring, the positive impact of carbon coating on Si/Gr composites was more noticeable.

Jia et al.^[137] manufactured a high porosity calender-compatible carbon-nanotube/Si/carbon microspheres. These porous particles can tolerate pressure over 200 MPa, similar to pressures for industrial electrode calendaring. The electrodes with a loading of 3 mAh cm^{-2} exhibited a specific capacity of 750 mAh g^{-1} , and about 92% capacity retention over 500 cycles. The both (un)calendered electrodes exhibited similar cycling stability. Over 120 cycles, the electrodes calendered to 1.2 and 1.4 g cm^{-3} demonstrated capacity retentions of 96 and 91%, with volumetric capacity densities of 844 and 980 mAh cm^{-3} , respectively. The end-of-life swelling of the calendered electrodes was estimated from electrode thickness changes before and after cycling, which were about 34% and 45% after 120 cycles for the electrodes calendered to 1.2 and 1.4 g cm^{-3} , respectively. The me-

chanical resilience of carbon nanotube/Si/carbon particles was measured by in situ atomic force microscopy (AFM) and SEM. Xu et al.^[138] produced Si/graphene/carbon nanotube (CNT) composites with a 3D, spherical porous structure using in situ growth of spheres of graphene and CNTs around Si particles. The particles have high electrical conductivity and mechanical strength, which can be compatible with the high-pressure calendaring process over 100 MPa. In contrast, the particles in the compressed electrode preserved their spherical shape. The calendered electrodes after five cycles showed a volume expansion of about 18% after lithiation, suggesting an ability to withstand the stress created during cycling. The lithiated electrode with a calendered density of 0.64 g cm^{-3} exhibited a volumetric capacity of about 1000 mAh cm^{-3} . Additionally, these anodes demonstrated a reversible capacity of 900 mAh g^{-1} after 700 cycles (90% capacity retention).

Wu et al.^[139] manufactured a Si/3D carbon composite anode material with good electronic and ionic conductivity using a proton exchange technique. This porous structure withstands the high-pressure calendaring process, while providing space for volume change of the Si nanoparticles during the (de)lithiation processes. This porous structure also provides many ion diffusion channels and reduces lithium ion diffusion path, thus showing higher lithium ion transfer numbers. The calendared electrodes showed an excellent cycling performance of 1600 mAh g⁻¹, with capacity retention of 75% at 2 A g⁻¹ after 1000 cycles, and an extraordinary rate capability of 1056 mAh g⁻¹ at 10 A g⁻¹.

SiO₂-based anode materials could also be used in LIBs, owing to their high theoretical capacity, better cycling stability than pure Si, abundance, and environmental friendliness. Nevertheless, low CE and irreversible capacity losses during cycling are the main challenges in using this anode material for commercial cells. Buga et al.^[140] investigated the effects of the amount of carbon and also calendaring process on the porous SiO₂/carbon composites. The optimized calendared electrode showed the best cycling stability, with a specific capacity of 715 mAh g⁻¹, higher CE, and the lowest charge transfer resistance during 200 cycles. **Table 1** shows the comparison of some calendared anode electrodes reported.

4.1.4. Lithium Titanium Oxide

Spinel lithium titanium oxide (Li₄Ti₅O₁₂, LTO) is an anode material of LIBs with a specific capacity of 175 mAh g⁻¹. LTO is well-known for its low reactivity with common electrolytes, intense volume changes, and high voltage plateau of 1.55 V (vs Li/Li⁺).^[141–143] The effect of calendaring on the LTO anode has been investigated. For example, Acharya et al.^[144] investigated the influence of calendaring on the charging rate of LTO electrode anodes. LTO was coated on an aluminum foil current collector, the electrodes were calendared with thickness reductions from 10% to 42%. For the electrode with a 42% thickness reduction, the thickness was changed from 175 μm (uncalendered electrode, 1.05 g cm⁻³) to 100 μm (1.76 g cm⁻³), and it demonstrated good capacity retention at 5C, although it exhibited faster capacity fade compared to the uncalendered and 10% calendared electrodes. Gockeln et al.^[145] studied the influence of two electrode fabrication methods: lamination and doctor blade techniques for LTO/carbon composites. They studied the effect of lamination pressures (varied from 1.5–3.3 MPa) on the microstructure, and resulting electrochemical performance of the electrodes. The laminated electrodes demonstrated higher specific capacities than both (un)calendered blade-cast electrodes, however, the cycling stability was similar for laminated and calendered electrodes.

Overall, anode electrodes have volume expansion during lithiation process, therefore, for the most cases the anode electrodes should have more porosity than cathode electrodes, and calendaring may take more optimization, the calendaring degree strongly depends on the type of anode active material, binders and electrode thickness and compositions. For instance, the electrodes with intercalation mechanism active materials (Gr and titanium oxides) can be calendared to higher densities, with relatively lower porosities, compared to the electrodes made with alloy-

(Si, germanium, and tin), and conversion- (transition metal oxides, such as Fe₃O₄, Co₃O₄, CuO, etc.) mechanism active materials, that need more porosity, because of having significant volume expansions during dis(charging) processes. Hence, for every electrode, the optimum condition of calendaring should be determined based on the selected active material.

4.2. Performance of Calendared Cathodes

Calendering of cathodes serves a somewhat different role from the calendaring of anodes, as CAM are typically more limited in intrinsic conductivity, which must be thus compensated by strong interactions between the CAM and the conductive carbon network. From work in electrochemical impedance spectroscopy (EIS) and modeling it has been seen that a variety of parameters, including the intrinsic properties of the CAM, the structure of the oxide particles and the interface between the oxide particle and the carbon network all have a significant influence on the performance.^[61,65,70,75,146–149] For this reason, it is important to better understand the properties of different CAMs and how the calendaring processes of cathodes based on these CAMs impact the electrode morphology, material properties, and electrochemical performance.

4.2.1. Lithium Iron Phosphate

Lithium iron phosphate (LiFePO₄, LFP) is an attractive CAM for commercial applications due to its low cost, low toxicity, high stability, high safety and theoretical capacity (170 mAh g⁻¹), and long-term cyclability.^[150–155] However, despite its many advantages, LFP still suffers from intrinsic limitations because of its poor electrical conductivity and sluggish Li⁺ transport.^[150,151] Common methods to overcome these challenges are fabricating nanoparticles,^[156] using specialized conductive coatings,^[151] use of blended cathodes,^[157,158] or implementing 3D foam current collectors.^[150,156] These methods can add costs or extra process steps, resulting in less cost-effective production. By calendaring the LFP electrodes during electrode production, the mechanical contact between the CAM, the binder and the conductive additive improves, and thus the electrochemical performance is improved.

Work by Lu et al.^[159] on LFP cathodes, with Gr and CB as the conductive additives, and a PVDF binder, investigated the impact of calendaring on the electrode properties and electrochemical performance. In this study, the LFP cathodes before and after calendaring had porosities ranging from 34% to 55% and demonstrated significantly different resistances of 40 and 1.5 Ω, respectively. Oladimeji et al.^[28] showed a similar effect of calendaring on LFP cathodes with PVDF and CB, where the charge transfer resistance measured by EIS was improved from 182.4 to 157.8 Ω after calendaring. Kannan et al.^[155] demonstrated the improvement in electrochemical performance of LFP cathodes, based on LFP, carbon (conductive carbon (3%) and super P (3%)), and PVDF, after calendaring with multiple different separator types. Bommel et al.^[30] showed that both the contact resistance and the electrochemical performance could be improved by calendaring LFP cathodes. Sousa et al.^[152] demonstrated an improvement in discharge capacity after calendaring for rates up to 5C (from 27.4

Table 1. Literature comparison of composition, and electrochemical performance of anode electrodes before and after calendaring (Cal.).

Anode	Electrode composition [wt%]	Density [g cm ⁻³] before/after Cal.	Porosity [%] before/after Cal.	First cycle capacity before/after Cal.	Cycling life before/after Cal.	Ref.
Graphite (Gr)	Gr: CA: PVDF: (88:4:8)	0.96/1.36	56/38	Similar 2.5 mAh g ⁻¹ at 0.05C	similar, 2 mAh cm ⁻² after 300 cycles at 1C	[21]
	Gr: CA: PVDF: (92:2:6)	-	NA/40	NA/340 mAh g ⁻¹ at 0.1C	similar, 330 mAh g ⁻¹ after 15 cycles at 1C	[96]
	Gr: CA: CMC: SBR: (92.5:3.5:1.5:2.5)	-	-	Similar about 310 mAh g ⁻¹ at 0.1C	similar, 300 mAh g ⁻¹ after 120 cycles at 0.1C	[99]
	Gr: CA: PAA: PTFE: (90:2:8:40)	-	50/30	Similar about 300 mAh g ⁻¹ at 0.1C	NA/240 mAh g ⁻¹ after 120 cycles at 2C	[101]
Silicon	Si nanoparticle: CA: PAA (75:10:15)	-	-	Similar about 1750 mAh g ⁻¹ at 0.1C	862/1370 mAh g ⁻¹ after 100 cycles at 0.1C	[111]
	Si:graphite:CB: polyimide: (43.3: 24.2:19.3:13.2)	-	NA/20-25	Similar about 2240 mAh g ⁻¹ at 0.2C	similar, 1680 mAh g ⁻¹ after 50 cycles at 0.2C	[110]
SiO	SiO/C: Polymer: (90:10)	0.83/1.28	63/43	Similar about 3 mAh cm ⁻² at 0.1C	2/3 mAh cm ⁻¹ after 120 cycles at 0.1C	[118]
Si/Fe-Mn alloy	Si-alloy: Gr: CA: polyamide: (15:76:1:8)	-	-	similar, 600 mAh g ⁻¹ at 0.1C	similar, 600 mAh g ⁻¹ after 100 cycles at 0.1C	[119]
Si-alloy/graphite	Si-alloy/ Gr: CA: lithium polyacrylate (LiPAA): (75:5:25)	0.98/1.25	NA/35	similar, 950 mAh g ⁻¹ at 0.1C	similar, 950 mAh g ⁻¹ after 50 cycles at 0.1C	[120]
Si/carbon /Gr	Si/C: CA: CMC: SBR: (80:5:12:3)	0.5/1.3	-	similar, 600 mAh g ⁻¹ at 0.2C	similar, 600 mAh g ⁻¹ after 30 cycles at 0.2C	[127]
	Si/C/Gr: CA: CMC: SBR: (94:1:2:2)	NA/1.6	60/27	similar, about 660 mAh g ⁻¹ at 0.5C	NA/630 mAh g ⁻¹ after 50 cycles at 0.5C	[135]
Si/carbon/CNT	Si/C/Gr: CA: CMC: SBR: (90:4.6:3.6:1.8)	0.8/1.45	63/33	similar, about 600 mAh g ⁻¹ at 0.5C	similar, about 540 mAh g ⁻¹ after 120 cycles at 1 mA cm ⁻²	[136]
	Si:Gr: CMC: CA + KOH: (73.2:11:7.3:8.5)	0.6/1.5	70/30	Similar about 3500 mAh g ⁻¹ at 90 mA g ⁻¹	similar, 1400 mAh g ⁻¹ after 50 cycles at 600 mA g ⁻¹	[112]
	CNT/Si/C: CA: polyimide: (80:5:15)	0.8/1.8	-	NA/660 mAh g ⁻¹ at 0.5C	NA/1300 mAh g ⁻¹ after 1500 cycles at 1 mA cm ⁻²	[137]
CNT/Si/C: CA: PVDF: (80:10:10)	CNT/Si/C: CA: PVDF: (80:10:10)	NA/0.64	-	NA/1600 mAh g ⁻¹ at 0.2 A g ⁻¹	NA/1000 mAh g ⁻¹ after 700 cycles at 2 A g ⁻¹	[138]

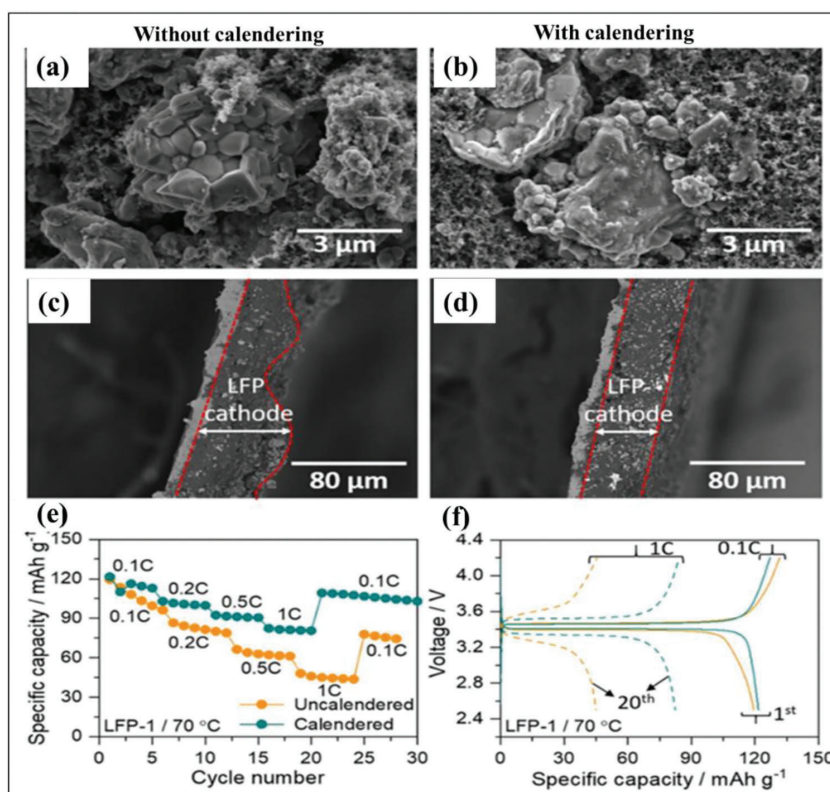


Figure 12. LFP cathodes: a,b) SEM images, c,d) cross-sectional SEM images, e,f) comparative rate capability and charge/discharge curves of Li/SPNE/LFP cells measured at 70 °C. Reproduced with permission.^[161] Copyright 2022, Springer Nature.

mAh g⁻¹ to over 80 mAh g⁻¹), for LFP cathodes prepared using screen-printing methods and an LFP-based ink. Besnard et al.^[157] explored the impact of calendaring on both pure LFP cathodes and blended NMC/LFP cathodes, and for both of them, it was demonstrated that the conductivity experienced only a slight increase (0.3 to 0.6 S m⁻¹ in the case of the LFP electrode mixture) after calendaring while the contact resistance significantly decreased (from 36 to 0.8 Ω cm² for LFP cathodes). There is, however, a trade off in electrode properties, as shown by the work of Yu et al.^[160] where the increase in cathode density after calendaring led to a decrease in capacity. However, in both cases the energy density must be considered, which is improved upon calendaring. For example, in the case of Yu et al., the density was increased from 1.55 to 2.2 g cm⁻³, corresponding to an improvement in volumetric energy density of about 42%, while the loss in specific capacity (≈111 mAh g⁻¹ to ≈87 mAh g⁻¹) by going to higher densities was only about 22%.

Calendaring can also play a role in improving performance for novel LFP cathode types. Erabhoina et al.^[161] demonstrated for all-solid-state batteries (ASSBs) based on LFP cathodes, composed of LFP, CB, PEO, and LiTFSI, that the density and homogeneity of the cathode could be increased after calendaring, as demonstrated in **Figure 12**, resulting in an increase in the discharge capacity delivered (82 mAh g⁻¹ for the calendared cath-

ode, compared to 47 mAh g⁻¹ for the uncalendared). Calendaring was also applied to LFP-based ASSBs by Helmers et al.^[162] and they showed that direct calendaring led to an increase in electrical conductivity, but decrease in ionic conductivity, while calendaring during the extruder process led to increase ionic conductivities. Yang and Joo et al.^[150] also demonstrated that highly structured cathodes (in this case, LFP on a NiCrAl-alloy foam) also benefit from calendaring as the cathodes showed significant improvements in the kinetics after pressing. Besides ASSB applications, Napolskiy et al.^[163] applied calendaring to novel LFP cathodes that use CNTs as the conductive additive and demonstrated that high compression rates resulted in low porosity and poor rate performance due to poorer electrolyte wettability. However, they also demonstrated that the C-rate performance could be improved by increasing the roll temperature and found that high C-rate performance and good cycling stability could be achieved with a compression rate of 10% and roll temperature of 100 °C.

4.2.2. Nickel–Manganese–Cobalt-Oxides

Nickel manganese cobalt oxides (NMC) are by far the most popular CAM for high energy and high power LIB applications. These materials possess many advantages, including high energy den-

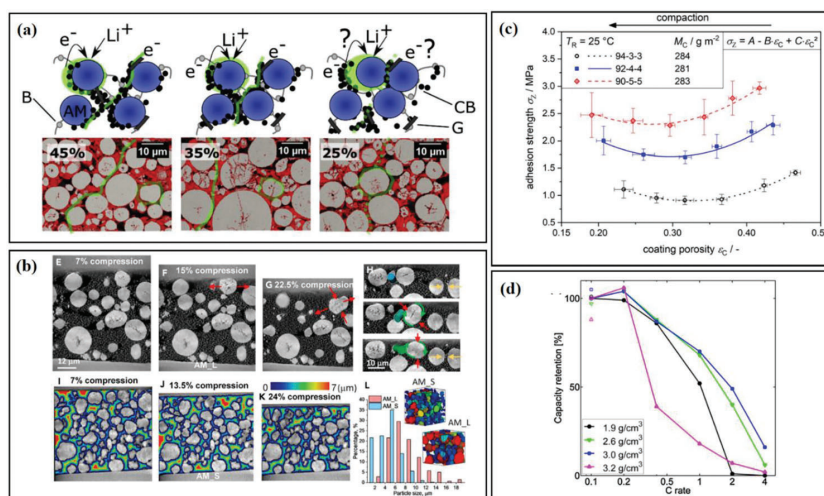


Figure 13. a) Schematic interpretation of charge transport processes in NMC cathodes with different porosities after calendaring, where blue spheres = AM, black spheres = CB, flakes = Gr and gray wires = binder. Green lines demonstrate electric pathways. In the SEM cross-sections, the red color illustrates the CBD. Reproduced with permission.^[166] Copyright 2016, Elsevier. b) In situ electrode compression experiment using X-Ray nano-CT and the microstructural evolution. E–G) Reconstructed virtual slices showing the microstructural change of the AM_L electrode under 7% (E), 15% (F), and 22.5% (G) compression, following a DSS procedure to include the deformation of CBD. Red arrows indicate the particle deformation. Structural self-arrangement (from top to bottom) via particle rotation and deformation (H). Yellow arrows indicate the compression of CBD. Details of the cylinders to characterize particle orientation are introduced later. I–K) Reconstructed virtual slices overlaid with color-map showing the change of the inter-particle gap under 7% (I), 13.5% (J), and 24% (K) compression of the AM_S electrode. Comparison of the particle size distribution between AM_S and AM_L (L). The standard deviation for AM_S and AM_L is 1.8 and 3.1 μm , respectively. The insets display the morphology of the color-coded particles, highlighting the average size difference. Reproduced with permission.^[169] Copyright 2020, Elsevier. c) The adhesion strength, σ_z , of cathodes with different compositions at constant mass loading (280 g m^{-2}) and roll temperature (25°C). Reproduced with permission.^[15] Copyright 2020, John Wiley & Sons. d) The capacity retention of NMC cathodes with different densities after calendaring at different C-rates. Reproduced with permission.^[182] Copyright 2017, Elsevier.

sity, high power density, high specific capacity, high rate capability, and good thermal stability.^[19,164,165] In the cathode, NMC is integrated into a conductive carbon network, composed of binders and conductive carbon, and in order to maximize the many advantageous properties of NMC, the morphology of the electrode must be optimized.

One of the most essential steps in cathode production is to ensure that the CAM has good contact with the conductive carbon network to enable efficient electron transfer. Bockholt et al.^[166] demonstrated this with cross-sectional SEM images where the contact between NMC and the carbon network was improved after calendaring (from a porosity of 45% to 35% and 25%) to establish efficient electrical pathways. In another study, Bockholt et al.^[167] also demonstrated that intensive dry-mixing of the NMC cathode materials mixture could result in loss in electrical contact within the electrode coating, due to coating of most of the conductive additive onto the CAM surface. These contacts could be re-established by calendaring, resulting in strong cycling stability, with no capacity loss after 400 cycles at 1C, and improved C-rate performance up to 5C. This is schematically demonstrated in Figure 13a, including SEM cross-sectional images, for NMC cathodes produced with different densities after calendaring. Improved C-rate performance was also observed by Parikh et al.^[16] after reduction of the porosity from 50% to 35%, an effect attributed to shortened Li^+ diffusion lengths. In a study by Westphal et al.,^[23] calendaring of NMC cathodes (composed of CB (5%) and PVDF (5%)) with line loads of up to 468 N mm^{-1} , cor-

responding to a density increase from 2.25 to 2.95 g cm^{-3} , resulted in a significant decrease in the electrode resistivity. Haarmann et al.^[168] also investigated the impact of calendaring on NMC622 cathodes (PVDF (2.25%) and CB (1.5%) and Gr (0.75%)) with varying solids content in the dispersion (65 vol%, 70 vol%, 75 vol%, and 80 vol%). They found that the electrical resistance was highest for both the highest and lowest solid contents, and could be significantly reduced for all solids contents by calendaring.

51–High compaction can increase the ionic resistance, therefore, it may negatively impact the electrochemical performance. A detailed X-ray nano-CT study by Lu et al.^[169] explored the interplay between electrode thickness, porosity and density after compression for NMC electrodes up to 24%. Their results are demonstrated in Figure 13b. They found that for electrodes composed of larger particles, calendaring can worsen pre-existing microstructural heterogeneities, leading to limited C-rate performance, while for electrodes composed of smaller particles, the deformation due to calendaring was much more homogeneous, the tortuosity lower, and thus these electrodes showed a higher rated capacity. In general, in this study, the performance at high C-rates was worse for the NMC cathodes after calendaring. However, the highest cathode porosity in this study was only 35.4% (uncalendar), which likely contributed to the limited rate capability.

The mechanical challenges of NMC when compacted were compensated for by Kim et al.^[170] through combining a high-

mechanical-strength single-crystalline NMC with a polycrystalline NMC. They found that particles with low mechanical strength found in the upper layer of the cathode can be fractured during calendaring. By creating a double-layer cathode with high mechanical strength, single-crystalline NMC making up the upper layer, this fracturing effect was completely prevented. A study by Klemens et al.^[171] examined the influence of calendaring on cathodes containing a porous, structured NMC111 and a compact NMC111. They found that the porous NMC111 cathodes required a higher compaction factor, but the resistivity was reduced by 95%, while it was just 78% for the compact NMC111, although this could be improved with higher coating drying rates. Müller et al.^[172] also investigated the influence of calendaring on cathodes based on porous structured NMC111, and found that the porous NMC111 is capable of withstanding pressures up to 40% porosity without damaging the CAM pore structure.

Kuchler et al.^[173] analyzed the 3D microstructure with X-ray tomography to determine the influence of calendaring on NMC cathodes and found that significant changes in the morphology already occur for compaction loads of 300 MPa or higher, although no information about the line load was given. A study by Daemi et al.^[174] took the X-ray tomography investigation a step further and used 4D visualization to image battery electrodes undergoing compression in situ, and map the strain evolution and particle displacement. They found that strain was seen as concentrating throughout the point of the electrode where compression was applied and propagating toward the bottom, with this effect attributed to the high displacement of small particles fragments.

The content of inactive material in the cathode (namely binder and conductive carbon) can strongly influence the impact of calendaring.^[175] A study by Zheng et al.^[176] investigated the impact of calendaring on a $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ -based cathode with varying contents of PVDF and acetylene black (CB). They found that with low levels of inactive material (2% PVDF and 1.6% CB), calendaring could significantly reduce bulk electric resistances within the coating, without changing the charge-transfer resistance, however, with high levels of inactive material (8% PVDF and 6.4% CB), the charge-transfer resistance increased after calendaring. This is due to the strong decrease in porosity accompanying the calendaring of cathodes with high inactive material contents. Another study by Lenze et al.^[177] investigated the influence of CB contents (4% and 5.88%) on the performance of NMC cathodes after calendaring. They found that low CB contents show lower discharge capacities above C-rates of 0.2C, even after calendaring to a volume reduction of up to 22 %. The impact that calendaring has on the inactive material in the cathode must also be considered, as demonstrated in a study by Grissa et al.^[178] where they observed PVDF degradation in $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}]\text{O}_2$ cathodes (PVDF (2%) and CB (2%)) calendared to 27% and 21.2% porosity with a two-roll press at 80 °C. Investigation of the morphology of NMC cathodes by Rajendra et al.^[179] using X-ray microtomography showed a significant impact on the conductive carbon domain, suggesting that this region is permanently deformed by calendaring (with 2 MPa calendaring pressure). Another study by Meyer et al.^[15] investigated the impact of calendaring at different temperatures on $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathodes with NMC:PVDF:CB ratios of 94:3:3, 92:4:4 and 90:5:5, and found that increasing calendaring temperatures lead to decreasing porosities and line

load efforts due to the elastic deformation of PVDF, thus, lower PVDF contents lead to higher achievable porosity. However, adhesion strength increased with PVDF content and decreased with porosity until $\approx 30\%$, whereby it increased again. This relationship is demonstrated in Figure 13c. Diener et al.^[20] evaluated the deformation behavior of NMC622 cathodes during calendaring, whereby they directly measured the deformation using a direct-gap detection method, demonstrating again the influence of the inactive components in NMC cathodes. They found that the spring back effect was lowered with higher binder content (1.5 wt% to 4.0 wt% PVDF), due to plastic deformation, and with higher mass loadings (20.1 to 35.4 mg cm^{-2}), due to the space for particle rearrangement. A study by Primo et al.^[180] examined the influence of both calendaring pressure and temperature and found that while the porosity and mechanical properties mainly depend on the applied pressure, the electrodes' conductivity mainly depends on the temperature, likely due to deformability of PVDF increasing with temperature. This is reinforced by the fact that the correlation between conductivity and calendaring temperature was better for measurements taken after electrolyte infusion, due to polymer swelling effects.

Control of the porosity of the cathode coating can be critical for minimizing the cell impedance, as was observed by Trask et al.^[181] who calendared a $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ cathode with PVDF (4%) and conductive carbon, C45 (4%), reducing the porosity from $\approx 56\%$ to 34.5% and drastically reducing the cell impedance measured by EIS. Kang et al.^[182] also showed reduced cell impedance of NMC111 cathodes after calendaring from densities of 1.9 g cm^{-3} to 2.6 , 3.0 , and 3.2 g cm^{-3} , however the rate capability of these cathodes was significantly worse at 3.2 g cm^{-3} , as demonstrated in Figure 13d, and evidence of crushing of the NMC particles was seen. Similar behavior was observed in a study by Stein et al.^[183] where the calendared NMC111 cathodes initially showed improved discharge capacities and rate capabilities, however, for long-term cycling, the capacity fading was higher. This is likely due to the particle crushing phenomena, whereby the cracking of particles initially increases the electrochemically active surface area, but causes more SEI growth and particle breakage with further cycling. Particle breakage caused by calendaring can lead to higher moisture uptake, which can be detrimental to the electrochemical performance, as observed by Huttner et al.^[19] for NMC622 cathodes. The influence of calendaring on tortuosity can also be used to explain the detrimental electrochemical performance, as electrodes with higher densities typically possess higher tortuosities, which in turn inhibits ionic conductivity within the electrode due to longer ion diffusion distances.

Calendaring can also be used to enable thicker cathodes with higher energy densities. In a study by Du et al.^[184] thick NMC532 based cathodes (with mass loadings up to 25.4 mg cm^{-2}) produced using aqueous methods showed crack formation in the coating after drying, and demonstrated that the cracks in the coating could be reduced or removed by calendaring, which was accompanied by reduction in the internal resistance of the electrode. Hu et al.^[185] investigated calendaring of $\text{LiNi}_{0.7}\text{Mn}_{0.22}\text{Co}_{0.08}\text{O}_2$ cathodes with thicknesses of $132 \mu\text{m}$ before calendaring (areal loading of 22.41 mg cm^{-2}) and found that reduction of the porosity from 60% to 40% with calendaring improved the rate capability and capacity retention. Singh et al.^[186]

employed calendering to reduce the cathode thickness 10%, in order to enable the cycling of NMC111 cathodes at 0.5C with thicknesses up to 320 μm (loading weight of $\approx 72 \text{ mg cm}^{-2}$). Another study by Singh et al.^[187] studied the impact of calendering on NMC111 cathodes (composed of C65 (3%), Gr (3%), carbon fibers (1%) and PVDF (3%)) with a 300 μm thickness ($\approx 71 \text{ mg cm}^{-2}$), reducing the porosities from 44% to 38% and increasing the volumetric energy density at C/5 by 19%. They found that the NMC cathode with the lowest porosity demonstrated the best performance, however, this study modified the cathode and anode porosities simultaneously, so definitive statements about the influence of calendering on the cathode cannot be given. However, it can be stated that there is always a tradeoff between energy and power density, as Heubner et al.^[188] showed in their study of NMC622 cathodes with thicknesses ranging from 129 to 212 μm and porosities from 34% to 43%. They demonstrated that while energy density increases with increasing thickness and decreasing porosity after calendering, the charge transfer resistance also increases, leading to poor C-rate performance. They also observed the deformation and cracking of particles using high line loads (1000 N mm^{-1}). Hu et al.^[185] investigated calendering of $\text{LiNi}_{0.7}\text{Mn}_{0.22}\text{Co}_{0.08}\text{O}_2$ cathodes with thicknesses of 132 μm before calendering (areal loading of 22.41 mg cm^{-2}) and found that reduction of the porosity from 60% to 40% with calendering improved the rate capability and capacity retention. Some select electrochemical results from the literature for cathodes before and after calendering are shown below in Table 2. The limited entries and information displayed in this table reflect the need for more electrochemical-based calendering studies, as well as standards for which metrics to report.

Calendering has also been employed for producing cathodes containing non-traditional cathode binder materials (such as CMC), demonstrating its utility for enabling novel production processes (e.g., aqueous based). In a study by Loeffler et al.^[189] NMC111 cathodes were produced using aqueous dispersions with CMC (5%) and Super C45 (5% and 7%, corresponding to mass loading of 7.5 and 3.3 mg cm^{-2} , respectively) and the impacts of calendering were investigated. They found that calendering of the high energy density cathode, using calendering forces which corresponded to density changes from 1.49 g cm^{-3} to 1.66 and 1.88 g cm^{-3} , respectively, led to lower capacity fading at 1C after 70 cycles.

The application of calendering can also serve to improve the properties of NMC cathodes produced using non-traditional methods. In a study by Sliz et al.^[190] screen-printed NMC523 and NMC88 cathodes, where NMP was replaced with DMF, were produced and it was found that calendering reduces the roughness and improves the long-range electrical contact in the coating. Xiong et al.^[191] produced NMC532 cathodes with an oriented pore structure using a NH_4HCO_3 foaming agent and showed improved C-rate performance after calendering (with capacity retention of 67.6% at 5C).

Although the influence of calendering on NMC cathodes has been studied more than any other cathode material, the majority of these investigations were done at the lab scale, which must be taken into consideration when thinking of upscaling the process. Additionally, many of these studies had limited electrochemical investigations and to better understand the interaction between calendering processes, resulting electrode microstructure

and electrochemical performance, more rigorous electrochemical studies are necessary, especially for up-scaled processes. That being said, a few points regarding calendering of cathodes can already be stated:

- 1) Calendering can be a critical step to ensure electronic transfer process in the cathode coating, due to the limited intrinsic electrical conductivity of most CAMs.
- 2) High calendering strengths can result not only in highly dense cathodes, which are accompanied by charge transfer limitations, but also in particle breakage, which can lead to higher moisture uptake, more active sites for electrolyte side reactions and pulverization of the CAM during cycling.
- 3) The amount and distribution of the inactive components in the cathode (namely binder and conductive additive) influence the effectiveness of calendering.

4.2.3. Lithium–Nickel–Aluminum-Oxides

Lithium nickel (cobalt or manganese) aluminum oxides (NCA and NMA) are common CAMs for LIB applications due to their high theoretical capacity and good cyclability at room temperature.^[192] However, Ni-rich cathodes can be subject to extreme capacity fading owing to CAM particle cracking and breakage during long-term cycling.^[193] Compaction of the cathodes via calendering can improve the electronic percolation network and volumetric energy density, however, for NCA, over-compaction can destroy the mechanical properties, facilitate particle cracking and restrict electrolyte wetting.^[193] It is vital to optimize the calendering approach for this material.

Lu et al.^[194] investigated the impact of calendering on $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) cathodes, prepared with Gr, CB and PVDF, with varying thicknesses and demonstrated that improved coating uniformity could be achieved after calendering. Bobrikov et al.^[192] also studied $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) cathodes to investigate the impact of calendering on the abnormal phase-separated structural behavior of NCA during the initial charge cycle. It was demonstrated that stronger compaction partially suppresses the phase separation of NCA and causes partial destruction of the NCA agglomerates, which improves the ion transport characteristics. A study by Sarawutanukul et al.^[193] on $\text{LiNi}_{0.88}\text{Co}_{0.09}\text{Al}_{0.03}\text{O}_2$ (NCA) employed calendering processes to optimize the electrode properties. They observed a decrease in NCA crystallite size after calendering, which can contribute to an accumulation of strain on the particle and decrease the capacity retention capabilities. However, they showed that with optimal compaction degree (of 17.54%) and particle rearrangement, high C-rates and high capacity retention could be achieved.

From a study by Haselrieder et al.^[195] a high power lithium manganese spinal ($\text{Li}(\text{Li-Mn-Al})_2\text{O}_4$) that was sensitive to mechanical stresses could be enabled by blending it with NCA ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$), allowing it to be subjected to calendering, which improved the specific discharge capacity for C-rates up to 6.5C. A study by Meyer et al.^[37] investigated the influence of calendering on two different NCA cathodes. They found that the cathode containing a blend of NCA with smaller NCA particles had a more distinct porosity decrease at low line loads compared to the NCA cathode with larger NCA particles. The breaking

Table 2. Comparison of cycling capacities before and after calendaring for select NMC cathode examples from the literature.

Anode	Electrode composition [wt%]	Density [g cm ⁻³] before/after Cal.	Porosity [%] before/after Cal.	First cycle capacity ratio before/after Cal.	Cycling capacity ratio before/after Cal.	Ref.
Gr	NMC/C45/CMC: 88/7/5	1.49/1.66 and 1.88	-	≈131/≈134 mAh g ⁻¹ (1.88 g cm ⁻³) at 1C	≈122/≈127 mAh g ⁻¹ (1.88 g cm ⁻³) after 70 cycles at 1C	[189]
Li	NMC/PVDF/CB: 94/3/3	1.9/3.0	≈60/≈39	≈132/≈126 mAh g ⁻¹ after at 0.1C	≈19/≈87 mAh g ⁻¹ at 1C and 0/≈87 mAh g ⁻¹ at 4C	[182]
Li	NMC/PVDF/C65/Gr: 94.5/3/1.67/0.83	-	32.5/18.8	≈173/≈168 mAh g ⁻¹ after at 0.2C	≈78/≈74 mAh g ⁻¹ at 3C and ≈127/≈126 mAh g ⁻¹ at 5C	[169]
Li	NMC/PVDF/Super P: 96/2/2	-	60/40	≈202 at 0.1C for both	≈180/≈200 mAh g ⁻¹ at 0.1C after 24 cycles and ≈100/≈165 mAh/g at 2C	[185]
Li	NMC/CB/Gr/PVDF: 95.5/1.5/0.75/2.25	2.6/2.8 and 3.2	33.86/30.20 and 20.55	-	≈60 and ≈45 mAh g ⁻¹ at 1C after 30 cycles; ≈160 mAh g ⁻¹ at 0.1C after 65 cycles for both (2.8 and 3.2 g cm ⁻³)	[19]
-	NMC/CB/PVDF: 90/6/4	2.06/2.73 and 2.21/2.74	-	≈117 mAh g ⁻¹ and ≈115 mA g ⁻¹ after 27 cycles	≈92 and ≈88 mAh g ⁻¹ at 5C; ≈117 and ≈108 mAh g ⁻¹ at 1C after 430 cycles	[167]
Li	NMC/CB/Gr/PVDF: 89.29/3.57/3.57/3.57	-	50.6/40 and 67.7/40	≈140/≈145 mAh g ⁻¹ and ≈150/≈150 mAh g ⁻¹ at 0.5C	≈20/36.67 mAh g ⁻¹ and 55.34/85.36 mAh g ⁻¹ at 5C	[171]
Gr	NMC/CB/PVDF: 90.2/5.88/3.02	Calendering degree 0%/10%/22%	-	-	≈99/≈80/≈122 mAh g ⁻¹ at 2C; ≈10/≈7/≈27 mAh g ⁻¹ at 5C	[177]
Li	NMC/CB/PVDF: 96/2/2	-	21.2 and 27.0	162 mAh g ⁻¹ at 0.1C for both	≈115 and ≈140 mAh g ⁻¹ at 0.1C for both	[178]

strength of this blended NCA was also slightly lower than NCA without the small particles, despite the fact that the smaller NCA particles possessed higher densities. Sim et al.^[196] studied the effects of calendaring on $\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Al}_{0.05}\text{O}_2$ (NMA) cathodes and proposed that calendaring could reduce the pulverization of NMA particles for repeated electrochemical cycling, resulting in an overall improvement in capacity retention.

4.2.4. Lithium Cobalt Oxide

Lithium cobalt oxide (LiCoO_2 , LCO) was a popular CAM due to its high tap density, high ionic conductivity, high discharge plateau voltage, and high theoretical capacity.^[197,198] To enable the high voltages of LCO, however, the material will be subjected to voltages beyond 4.2 V, where it can undergo side reactions and loss of Co and O, leading to particle breakage and ultimately limiting the long-term cycling stability.^[198]

In a study by Fa and Fedwik,^[199] LCO cathodes were subjected to calendaring, and showed that the specific capacity could be improved by compaction with 27 MPa and further improved with compaction at 54 MPa. An improvement in the C-rate capability was also observed. In a study by Ebner et al.,^[43] calendaring of non-spherical LCO particles was compared to NMC particles, and significantly higher tortuosity anisotropy was observed from LCO, however, not much difference in the particle alignment for LCO was seen after calendaring for pressures of 30, 60, and 200 MPa. Lim et al.^[201] studied calendered LCO particles with packing densities of 2.2 to 3.6 g cm^{-3} . They observed that with increasing packing density, the porosity, contact resistance, SEI resistance, and charge transfer resistance all decreased while the specific surface area and tortuosity increased. The discharge capacities were also improved (from 140 to 148 mAh g^{-1}) at 0.1 C for densities of 2.2 and 3.6 g cm^{-3} , respectively, and these positive effects are enhanced at 1C.

Although calendaring cannot address all the challenges of LCO cathodes, it can offer one possible solution to improve cycling performance. When combined with additional strategies, such as CAM coatings, the electrochemical performance can be further optimized.

4.2.5. Lithium Nickel Oxide

Despite its low operating voltage than other transition metal oxides, lithium nickel oxide (LiNiO_2 , LNO) is a good CAM candidate due to its high-temperature stability, low self-discharge, high specific capacity, and certainly, a low-cost cathode compared to Co-containing CAM.^[201–203] One of the major challenges of LNO is the anisotropic volume change during charge/discharge, which can result in micro crack formation and eventual particle pulverization.^[202,203]

Fan and Fedkiw et al.^[199] studied the impact of calendaring of LNO cathodes on the electrochemical performance and compared to LCO and LMO cathodes. They found that while the capacity of LNO could be improved for compaction up to 27 MPa, the rate capability was much more limited than LMO and LCO cathodes. In a study by Hamam et al.,^[205] LNO and 3% Al-doped LNO were subjected to mechanical testing to determine their

ability to withstand calendaring stress. It was shown that the structural integrity of the LNO particles was maintained with 100 MPa of compaction, but experienced breakage after 500 MPa. A real mechanical benefit was difficult to see from Al doping, however, after cycling at C/5 for 5 cycles, capacity retention of 95.5% was seen, compared to 77.6% for the undoped LNO. Similar improvements in capacity retention were observed for doping with tungsten (W), along with improvements in the ability to withstand compaction pressures.

Due to its extensive limitations, LNO has not been widely studied, as transition metal-doped LNO materials (such as NMC) offer much better performances.^[203,205] However, more popular Ni-rich CAMs still suffer similar limitations to LNO, so it is crucial to better understand how mechanical processing can improve the electrochemical performances of these materials.

4.2.6. Lithium–Manganese Oxide and Lithium–Nickel–Manganese Oxide

Lithium manganese oxide (LiMn_2O_4 , LMO) is a well-known CAM due to its theoretical capacity (148 mAh g^{-1}), low-cost and environmentally friendliness.^[35,206] However, for long-term cycling LMO possesses limited cycling stability- due to Jahn-Teller distortions,^[207] structural fatigue and particle cracking. Additional loss of active Mn can lead to capacity fading and reduced electrical conductivity.^[35] Due to the limitations of LMO, it is often combined with Ni ($\text{LiMn}_x\text{Ni}_y\text{O}_4$, LMNO) to improve cycling stability.^[208,209] Calendaring offers an additional industry accessible method for improving cycling performance.

Schilcher et al.^[35] studied the influence of the calendaring step on the electrode structure and electrochemical performance of LMO cathodes. They observed that an improvement in the electrochemical performance for LMO cathodes was seen for compaction rates up to about 25%, corresponding to optimal densities around 2.0 g cm^{-3} and a line load of 158 N mm^{-1} . Beyond that, the particle breakage was too large, and more severe capacity fading was observed. Lenze et al.^[177] also investigated calendaring of LMO cathodes and showed significant improvements in the specific discharge capacity up to 5C for 15% and 30% calendaring rates, especially for LMO cathodes with a CB: binder ratio > 1. If the long term cycling stability challenges of LMO can be solved, its high C-rate performance makes it a promising candidate for LIBs. He et al.^[210] successfully applied calendaring to a lithium-rich, manganese layered oxide ($\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.26}\text{O}_2$) cathode, a material associated with electrode compacting problems and high capacity loss in long term cycling, by infusing a near-zero-strain $\alpha\text{-LiAlO}_2$ to the grain boundaries.

5. Calendaring of Lithium–Sulfur Battery Electrodes

Lithium–sulfur batteries (LSBs) have been considered promising high-energy-density secondary battery system with an energy density of 2572 Wh Kg^{-1} (2835 Wh L^{-1}),^[211] which is about four-fold higher than those of state-of-art LIBs. Although LSBs are well-known for practical high-energy density batteries, their volumetric energy density is not competitive with LIBs due to the high electrode porosity of most sulfur cathodes, which hinders their

commercialization. Additionally, the practicality of LSBs is hindered by many problematic issues, such as short cycle life and low sulfur content/loading, poor safety, and a high self-discharge rate because of the shuttling of polysulfide intermediates between the cathode and anode.^[212–214] After the formation of polysulfides in the first cycles, the initial electrode structure/morphology is changed. Due to dependence of the electrochemical performance of LSBs on the electrode conditions, the design of the macrostructure of the electrode is a controlling factor for the bulk production of electrodes. The calendaring process is one critical step that determines the macroporous structure, electrolyte/sulfur ratio, mechanical properties, and bulk density and conductivity of the electrodes.^[215–224] Some studies showed interesting results for calendered electrodes of LSBs.

For instance, Kim et al.^[215] have optimized electrode processing conditions, such as mixing conditions and calendaring at different temperatures. The mild mixing conditions and high-temperature calendaring helped to produce favorable pore structures and enhance electrochemical performance. Both (un)calendered electrodes demonstrated a capacity of 1000 mAh g⁻¹ at 0.1C. Also, stable capacity retention of 700 mAh g⁻¹ after 200 cycles at 0.5C, and higher rate capability for the calendered electrode was achieved. Zhai et al.^[216] developed a 3D electrode made of sulfur/nitrogen-doped porous graphene/CNT skeleton, and used calendaring of this electrode in order to obtain a high volumetric energy density of 850 Wh L⁻¹, which is over threefold higher than that of the uncalendered electrode (275 Wh L⁻¹). The electrode with a compression of 30% showed a high rate capability, over 40% capacity retention at 2C, mainly ascribed to the enhanced conductivity from 6.4 to 11.8 S cm⁻¹, and well-maintained macropores in the electrode. The results could be attributed to low sulfur content in the electrode (only about 22 wt%), which is far from the average loading of 50% in the literature.^[225]

However, Lu and co-workers^[217] designed electrodes with 4 mg cm⁻², and studied the effects of electrode porosity on the electrochemical performance of the electrodes using the calendaring process. The optimized electrode delivered a high energy density of over 1300 Wh L⁻¹. For an area of 1 cm² of the uncalendered electrode (120 μm thick) about 11 μL of electrolyte was necessary, whereas, only 4.7 μL was required for the same area of the calendered electrode (60 μm thick). Controlling electrode porosity can decrease the electrode volume and electrolyte amount needed for full electrode wetting. Therefore, increasing the electrolyte/sulfur/conductive carbon contact (three-phase contact between active material-conductive carbon-electrolyte)^[226] improves the battery performance and delivers a higher specific energy density electrode. Additionally, they used Li₂S₆ as an electrolyte additive to increase the wettability of electrodes when the thick electrode is used, resulting in enhancing cycling stability (≈80% for 200 cycles) even with a dense and high-loading electrode. Liu et al.^[227] used La_{0.8}Sr_{0.2}MnO₃ (6.5 g cm⁻³) as a sulfur host for high volumetric capacity cells. The calendered electrodes (pressed at 0.2 MPa) with a sulfur loading of 6.2 mg cm⁻² and electrolyte/sulfur ratio of 7 μL mg⁻¹ exhibited a cathode density of 1.69 g cm⁻³ and porosity of 21%, in an excellent volumetric energy density about 2700 Wh L⁻¹, compared to uncalendered one (0.98 g cm⁻³, 55%, 1787 Wh L⁻¹). The volumetric energy is comparable to the Ni-rich oxide cathode (1800–2160 Wh L⁻¹) of LIBs. However, further increasing compression during

the calendaring process showed that electrodes have lower discharge voltage and capacity, because of poor electrolyte wetting in the low porosity, resulting in decreasing energy density.

Feng et al.^[221] developed a method to fabricate sulfur-rich secondary particles by a scalable production, using hail-inspired nano-storm technology, and evaluated the calendaring compatibility and conductivity of these composites. They used an electrode microenvironment model to understand the role of calendaring-compatibility of the active material. A high areal capacity of 12 mAh cm⁻² at 1 mA cm⁻² is obtained with a super high loading of 14 mg cm⁻² in the coin cell tests. However, pouch cells with various sulfur loadings also delivered a high specific capacity of about 1300 mAh g⁻¹ for ten cycles. Besides the drying study of LSB electrodes, Titscher et al.^[218] investigated calendered electrodes with sulfur loadings of about 3 mg cm⁻², with different compression grades of about 5% to 50% (electrode density about 0.6–0.9 g cm⁻³). All calendered and uncalendered electrodes showed similar specific capacity at 0.05C to 1C. Nevertheless, the manufactured electrode with 50% compression exhibited higher energy density.

Xue et al.^[219] introduced Li_xMo₆S₈ as an interlayer when they developed sulfur cathode electrodes for LSBs. Interestingly, the Li_xMo₆S₈ interlayer, with its high electronic and ionic conductivities and extra capacity contribution, could enhance the volumetric energy density of the calendered electrode (4 mg cm⁻²) at a pouch-cell level. Their results exhibited that the cell with Celgard polypropylene separator (PP)@Li_xMo₆S₈ and a high sulfur loading cathode has an areal capacity of about 3 mAh cm⁻² at 1 mA cm⁻², with an outstanding retention of 93.1% over 100 cycles. Remarkably, the volumetric energy density of calendered electrode (85 μm) with PP@Li_xMo₆S₈ is about fivefold higher than the PP separator at 1 mA cm⁻². These results suggest that this interlayer facilitates the redox kinetics of the cathode electrodes with high density. Some of their results are shown in Figure 14a. Gröbmeyer et al.^[220] deeply investigated the effect of calendaring on the two types of electrodes manufactured by KS6 (Gr, 26 m² g⁻¹) and Super C65 (62 m² g⁻¹) conductive carbon. The uncalendered sulfur/Super C65 electrodes exhibited a rough surface with huge cracks formed during solvent evaporation. However, calendaring of electrodes makes a smooth surface without material agglomerates, removes the large cracks, and makes good contrasts between the sulfur and the conductive carbon. The KS6 with a 2D structure generates a better percolation path via encapsulating the sulfur particles completely, to enhance the accessibility of sulfur particles by the electrons. Also, the internal electrode resistance when KS6 is employed was reduced by 68% after calendaring, resulting in a better electrochemical performance than the electrode made by Super C65 (the internal electrode resistance decreased by 38%), which contacts the sulfur particles in a network of a few micrometers.

Niesen et al.^[222] developed sulfurized poly(acrylonitrile) cathode materials and made electrodes with 90 wt% active material content, with an areal loading of 2.7 mAh cm⁻². With increasing in density from 0.8 to 1.0 g cm⁻³ via calendaring, no change can be seen in the cells' rate performance and the long-term cycling test (which demonstrated a decay of ~8% (0.05% per cycle) after 400 cycles). Chien et al.^[223] doubled the capacity density of the sulfur-carbon composite electrodes with sulfur-loading up to 3.5 mg cm⁻² by calendaring at 50 °C. The Cai group^[224] opti-

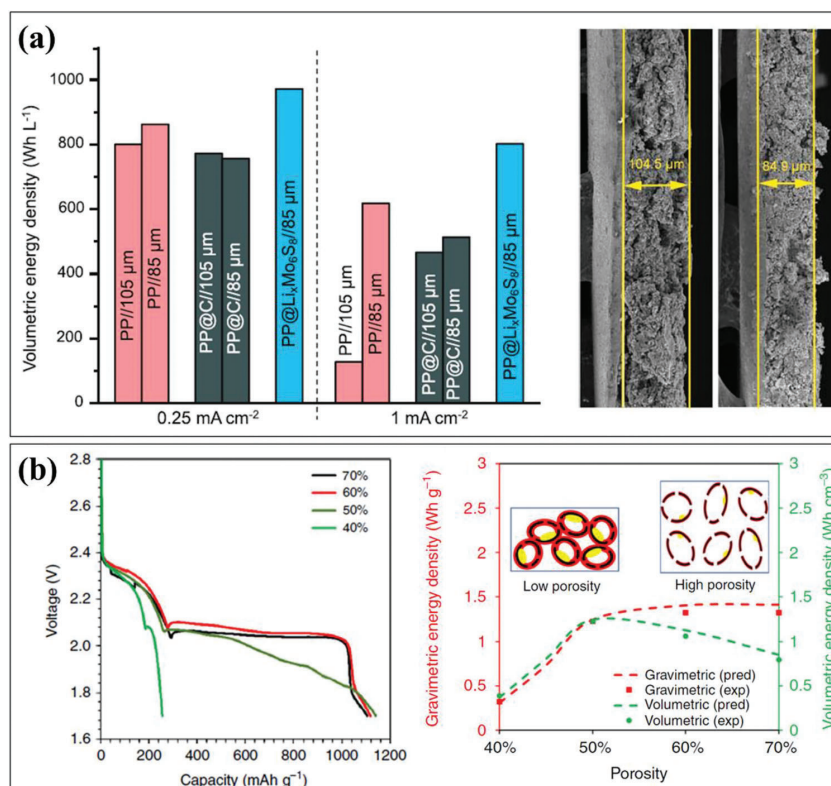


Figure 14. a) Effect of calendaring on sulfur/carbon (weight ratio of 6/4) cathodes with different separators: polypropylene@Li_xMo₆S₈ (PP@Li_xMo₆S₈), PP@carbon (PP@C), and pristine PP at 0.25 and 1 mA cm⁻², and also SEM images of sulfur/carbon electrodes before (105 μm) and after (85 μm) calendaring. Cathode electrode composition: 90% sulfur/carbon composite, and 10% PVDF. Reproduced with permission.^[220] Copyright 2019, Elsevier. b) The (dis)charge curves of sulfur/carbon (weight ratio of 80/20) cathodes with sulfur loading of 5 mg cm⁻² under different porosities, and the results obtained from the developed analytical model showed the correlations between the porosity of the cathode electrodes and energy densities. The electrode: sulfur/carbon composite/CB/carboxymethyl cellulose/styrene-butadiene rubber with a weight ratio of 76/18/3/3. Reproduced with permission.^[225] Copyright 2019, Springer Nature.

mized electrode porosity, and sulfur loadings of 2.5–5 mg cm⁻², to increase volumetric energy density to 500 Wh kg⁻¹ without sacrificing the sulfur utilization, which is restricted by the electronically accessible surface area of the carbon matrix. A typical two-plateau discharge behavior of an LSB at ≈2.4 and 2.1 V was observed when the porosity was higher than 55%, with an initial discharge capacity of about 1100 mAh g⁻¹. By reducing the porosity to 40%, the initial discharge capacity is only 250 mAh g⁻¹, signifying that electrodes with higher porosity obviously provide more reaction sites, and hence has a higher sulfur utilization rate. Based on their cell assembly and the results, electrodes with a porosity of 50–60% were recommended for a practical high-energy LSB design (Figure 14b). Table 3 reports studies regarding calendaring effect on the some selected electrodes of LSBs. To make a thicker sulfur cathode, the active material particles should be hard enough during calendaring to achieve a robust electrode and, thus, efficient conduction of ions and electrons.

6. Calendaring of the Other Type of Battery Electrodes

Jiang et al.^[228] studied the calendaring process on carbon-coated Na₃V₂(PO₄)₃ (NVP), as a most promising cathode of sodium-ion batteries,^[229,230] to explore the limitations in external ionic conductivity. They used two different sizes, 80 and 800 nm, for NVP, and the results showed a similar performance at high C-rates. The fast Na⁺ diffusion in the NVP/carbon composite structure suggests that NVP/carbon should be produced in a denser form (larger particles) to increase the tap density. They also showed that the performance of the NVP/carbon electrodes depends on more external electronic and ionic conductivities, which are unfavorably affected by calendaring and high areal loading. After calendaring, more than 50% of the electrode thickness was reduced, which reflects the main drawback of using nano-sized particles. The calendared electrodes demonstrated a significant drop in rate performance, and at 20C, dropped from 85%

Table 3. Literature comparison of electrode composition and electrochemical performance of sulfur electrode cathodes of LSBs before and after calendaring (Cal.).

Electrode composition [wt%]	Density [g cm ⁻³] before/after Cal.	Porosity [%] before/after Cal.	First cycle capacity [mAh g ⁻¹] before/after Cal.	Cycling life ratio before/after Cal.	Ref.
Sulfur/CB: poly(ethylene oxide): poly(vinyl pyrrolidone) (68:23:8:1)	0.6/1.1–1.7	-	Similar about 1000 at 0.1C	≈500/700 mAh g ⁻¹ after 150 cycles	[215]
Nitrogen-doped graphene (NG):sulfur:CNT (53:22:25)	-	-	Similar about 1100 at 0.5C	≈400/900 mAh g ⁻¹ after 180 cycles	[216]
Keijun black/sulfur composite (80 wt% S); CB: CMC:SBR (80:10:6:4)	-	64/29	Similar about 1100 at 0.1C	≈750/900 mAh g ⁻¹ after 200 cycles	[217]
carbon/sulfur composite (60 wt% S); CMC:SBR (90:5:5)	-	-	Similar about 1100 at 1C	≈200/700 mAh g ⁻¹ after 400 cycles	[219]
Sulfur/CB:PVDF (60:30:10)	-	-	Similar about 700 at 1C	≈180/450 mAh g ⁻¹ after 400 cycles	[220]
Co ₂ O ₃ /sulfur/carbon composite: CB: polyacrylic acid (80:10:10)	-	≈72/30	N.A./1350 at 1C	≈300/500 mAh g ⁻¹ after 110 cycles	[221]
sulfurized poly (acrylonitrile) composite: CB: CMC:SBR (90:5:2:3)	0.8/1.2	56/33	Similar about 1200 at 1C	≈similar 1100 mAh g ⁻¹ after 400 cycles	[222]
Carbon/sulfur composite (78 wt% of sulfur); CB: CMC:SBR (78:18:3:3)	-	70/55	Similar about 1000 at 1C	≈similar 1100 mAh g ⁻¹ after 400 cycles	[224]
Sulfur: Keijun black: CB: carbon nanofibers: poly(ethylene oxide): poly(vinylpyrrolidone) (65:21:3.5:3.5:5.4:1.6)	0.6/1.5	70/26	Similar about 1000 at 0.1C	≈similar 820 mAh g ⁻¹ after 100 cycles	[223]
Sulfur/La _{0.8} Sr _{0.2} MnO ₃ : CB: CMC:SBR (80:13:4:2:2.8)	0.98/1.69	55/21	Similar about 800 at 0.1C	NA/600 mAh g ⁻¹ after 120 cycles	[227]

(uncalendered) to 60% (calendered) because of a decreasing porosity and increased tortuosity, which hinders ionic diffusion.

The effects of calendering on Zn|MnO₂ batteries were also investigated on both Zn and MnO₂ electrodes.^[231,232] Calendering reduces the layer thickness of both electrodes and the micropore surface area of the MnO₂ cathode, which is a drawback for discharge capability and cycling life. The batteries with a calendered MnO₂ cathode showed about 40% lower discharge capacities than the uncalendered electrodes for identical discharge conditions. However, if only a calendered Zn anode was used with the uncalendered MnO₂, the discharge capacity was increased by about 25%.

Douard et al.^[233] studied the effect of electrode porosity on the electrochemical performance of MnO₂ symmetric supercapacitor devices in neutral aqueous electrolytes by electrode calendering. For whatever the mass loading (2–12 mg cm²), reducing the porosity from 70% (pristine electrode) to 50% (calendered electrode) enhanced the areal and volumetric capacitances. Reducing the porosity for electrodes with high-mass loadings by calendering could reduce the charge transfer resistance and increase the double-layer capacitance. Additionally, the electrode wetting property depends on the electrode loading and porosity. The calendered electrodes showed stable capacitance values compared to uncalendered ones, which proposes a faster wetting of the denser electrodes.

7. Conclusions and Outlook

In this review, the foundation of calendering processes and their underlying mechanisms were outlined. The link between the calendering process and the material-dependent structural response, and resulting performance is a crucial one. It was demonstrated how understanding this link can help to optimize calendering processes for a wide variety of AMs and applications, as well as allow calendering to be used to optimize material properties of electrodes.

Modeling and simulations can be a more accessible, cost-effective way to gain detailed understanding of microstructure, mechanical and electrochemical effects in the electrode, resulting from the calendering process. Connecting modeling approaches with experimental investigations is an important step to better understand the process-structure-performance relationship.

Calendering of cathodes can be key step in the production process to enable the necessary electron transfer reactions. However, knowledge of the microstructure and properties of the electrode, especially the CBD region and the CAM, is a necessary first step to choosing the appropriate calendering parameters to apply.

Anode electrodes, because of volume changes during (de)lithiation processes, should be very carefully calendered. The calendering degree strongly depends on the type of anode active material, binders, and electrode compositions. For example, the electrodes with intercalation mechanism active materials (graphite and LTO) can be calendered to higher densities, with relatively lower porosities, compared to the electrodes made with alloy- (Si, germanium, and tin), and conversion- (transition metal oxides) mechanism active materials. Therefore, for every electrode, the optimum condition of calendering should be determined based on the chosen active material.

The following conclusions can be generally applied to anode and cathode electrodes:

- 1) Calendering firmly controls electrode density and porosity; higher electrode density increases the volumetric capacity of cells. Lower electrode porosity decreases the electrolyte amount required for complete electrode wetting, which is critical in view of cost and gravimetric capacity density. The electrode porosity can strongly control the CE and cycle life of battery cells, especially since increasing the density can increase the ionic resistance.
- 2) Calendering may also decrease the internal electrical resistance of electrodes, increasing the conductive additive-active material contact, enhancing the electronic conductive pathways, and improving the rate capability.
- 3) Calendering affects the electrode tortuosity and wettability, which are critical for a high-performance and safe cell, influencing electronic pathways, ionic pathways, and determining the electrolyte filling step. For instance, in the sulfur electrodes, because of the insulating nature of sulfur, and consequent need for high electrolyte-sulfur-conductive carbon contact in the electrode, low porosity increases the electrochemical polarization and lowers sulfur utilization.
- 4) Calendering of electrodes smooths out the electrode's surface, removes large cracks, and enhances the contact between the active materials and the conductive additives. This allows for an optimization of the conductive network inside the composite electrode, thus increasing the overall electrical conductivity of the electrode.
- 5) The line load, the roll temperature, and the roll diameters in the calendering affect the adhesion strengths, and all three need to be optimized for target electrode compositions.
- 6) The calendering processing is critical for improving the structural stability of the active material and CBD in the electrode.
- 7) Dispersing conductive additive nano particles in the electrode after calendering also is a critical factor for having a better electrochemical performance.^[234]
- 8) Optimizing the calendering process for a given electrode composition is critical. Calendering electrodes without any optimization can lead to the following drawbacks: i) pore collapse after calendering, resulting in poor electrolyte wetting ability and ion diffusion; ii) damage of the hollow microstructure for some porous nanostructured active materials (like porous Si composites), in which case a gentle calendering process should be applied; iii) reduction of the three contact phases of electrolyte-active material-conductive additives,^[226] making electrolyte less accessible to the active materials, reducing the specific surface area of the electrode, and increasing the electrode tortuosity, and thus poor electrochemical performance of the electrode; and iv) in some cases, damage of the current collector if the calendering condition is not optimized for the electrodes.
- 9) The optimal calendered electrodes may have a less SEI formation than uncalendered electrodes, as the electrode porosity is reduced (the possibility of contacting active materials with electrolyte would be less). On the other word, with optimized calendering condition, the particle positions are altered, thus, changing in their shapes and structure should be minimum. Therefore, no effect on the atom scale can be concluded for

the optimal calendered electrode. However, applying a very high compaction degree on the electrodes to fabricate electrodes with high-density could damages particles and change their morphology particularly for porous particles.

Calendered electrodes are mainly tested in half-cells, and many of them exhibited outstanding mechanical stability upon cycling, however, their performance in a full-cell is often not investigated, especially with regard to energy density. Since batteries are dynamic systems where the performance of the electrodes are not independent from one another, more studies which focus on the influence that calendering of both the anode and cathode has on the overall battery cell system are required. Additionally, more studies should focus on evaluating the mechanical and electrochemical performance of calendered electrodes for full-cell tests, which also affects the CE and cycling performance. Calendering studies focused on novel materials, for example free-standing current collectors (such as carbon cloth), are also important to consider for future studies, as these novel materials will likely have a much different response to compression forces than traditional battery materials. In order to optimize performance for any application, the calendering condition for every electrode should be optimized, which is depending on active material morphology and structure, the true density of (non)active materials, particle size distribution of (non)active materials, binders, conductive carbon, mass loading, and double- or single-sided coating. For instance, (i) in the dry coating as a new technology, the size, morphology, and the amount of the binder (typically PTFE) are critical to control the porosity and density of the electrode. ii) If considering an active material, such as Si/carbon composites, the calendering optimization for every morphology should be certainly optimized. Therefore, no conclusion/optimal calendering condition can be provided for a material, for example NMC111, but, the optimized condition can specifically provided for a particulate NMC111, and specific binder and conductive carbon, which their abovementioned characterizations are known, also, importantly, the solid content in the slurry (for the wet electrode coating), and the amount of materials in the electrode composite effect on the optimal calendering condition, and with changing one single property, the calendering condition should be again optimised.

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Conflict of Interest

The authors declare no conflict of interest.

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