



Investigation on mechanical and microstructural evolution of lithium-ion battery electrode during the calendaring process

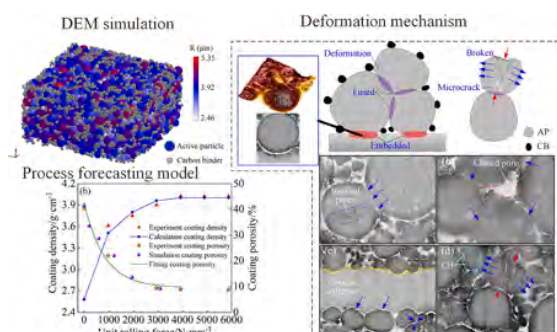
Junpeng Zhang, Huagui Huang^{*}, Jingna Sun

National Engineering Research Center for Equipment and Technology of Cold Strip Rolling, Yanshan University, Qinhuangdao 066004, China
College of Mechanical Engineering, Yanshan University, Qinhuangdao 066004, China

HIGHLIGHTS

- The discrete element method is taken to analyze the microscale and macroscale response.
- A predictive model is derived for the determination of the thickness and porosity.
- The deformation mechanism is summarized according to the electrode morphology.

GRAPHICAL ABSTRACT



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ABSTRACT

To increase battery capacity and improve electronic conductivity and electrochemical performance, lithium-ion battery electrodes are produced using a calendaring process. This work aims to reveal the evolution of mechanics and microstructure during the calendaring process, while a predictive model was derived to determine the thickness and porosity. Here, the discrete element method simulations and calendaring experiments were adopted to analyze the microscale and macroscale responses. A predictive model was supplemented using the Heckel equation. Furthermore, the electrodes were manufactured under incremental line load. According to the electrode morphology, the deformation mechanism was summarized: Particle pulverization, secondary particle fusion, binder network compression and the current collector's surface deformation. The increase of the electronic conductivity is related, on the one hand, to the conductive path inside the electrode being improved and, on the other hand, to the tightening of the contact between the coating and the current collector

Abbreviations: Lithium-ion batteries, LIBs; Active material, AM; Discrete element method, DEM; Carbon black, CB; Scanning electron microscope, SEM; Polyvinylidene fluoride, PVDF; Edinburgh Elasto-Plastic Adhesion, EEPA; Representative volume element, RVE.

^{*} Corresponding author.

E-mail address: hbg@ysu.edu.cn (H. Huang).

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1. Introduction

In the context of a sustainable modern society and climate goals, battery energy storage technology has emerged as an important direction for the transformation of the global automotive industry and the sustainable growth of the global economy. Lithium-ion batteries (LIBs) have become one of the main energy storage solutions in the consumer, power, and energy storage markets due to their long cycle life and high multiplier performance. Liu et al. introduced state-of-the-art manufacturing technology and analyzed the cost, throughput, and energy consumption based on the production processes [1]. There are still challenges in reducing the production cost and improving performance and durability. Therefore, it is necessary to gain insight into the effects of the production process on the battery and what special requirements the production process must be satisfied. Future trends and directions depend on not only changes in lithium-ion cell materials, but also the production process. The calendaring process ensures that the electrode achieves the desired compaction by presetting the gap size or the force between the two rollers at a suitable calendaring speed and temperature [2]. After coating and drying, the bonding strength between the coating and the current collector is low, and the particle spacing is large. According to Billot et al., the coating thickness and the calendaring represent the main influencing factors of the adhesion strength, enabling high-energy batteries with increased lifetime by modifying these characteristics [3]. Schmidt et al. provided important insights about the electrode microstructure, its evolution during densification, and the correlation to the electrochemical performance [4]. They show how different compaction rates must be balanced to maintain high (theoretical) energy density and high ionic conductivity, respectively, to maintain a fully developed pore network, which is necessary when the cell is operated at higher current rates. An optimal porosity must be found, which maximizes the electrochemical performance. Chen et al. pointed out that the carbon network microstructure is quite sensitive to electronic conductivity, especially for cathode electrodes [5].

To date, most of the studies have focused on the electrochemical properties of a lithium-ion cell. In contrast, little attention has been paid to the relationship between the calendaring process and the product structure. At the macroscopic scale, the “compaction resistance” parameter was proposed using the Heckle equation, a classical model in the field of powder compression, to construct a function between porosity or density and line load [6]. However, the actual conditions such as roller diameter, rolling speed, and contact friction are not considered, resulting in the inability to accurately analyze the coating structure and pressure distribution within the deformation zone. At the mesoscopic scale, the development of the tomography method is used to distinguish active material (AM), carbon-binder domain, and pore distribution and to reconstruct the 3D structure of the electrode. An X-ray nano-CT double-scan superposition technique was developed to build the full microstructure-resolved 3D model and elucidate the relationship between LIB performance and microstructural heterogeneities during the calendaring process, providing new insights into the electrode design and microstructure optimization [7,8]. Additionally, considering the complexity of experiments, numerical simulations have the unbeatable advantage of providing additional information and replacing complex experiments from a cost and time perspective. As an illustration, the discrete element method (DEM) simulations have been developed to provide insights into the interparticle contact during the calendaring process. Giménez et al. developed a DEM model for analyzing nanoindentation curves of the coating and reproducing the calendaring process while providing detailed information about the changes in the mesostructures and mechanical characteristics [9,10]. Although this deepens the understanding of the cathode indentation mechanism, the simulation results must be further validated. However, only active particles were considered in this model; the presence of binders was simulated by generating bonds between the active particles, which may break. For carbon black (CB), the investigation showed that

Table 1

Structural parameters of the uncalendered electrodes: composition, thickness, density, porosity, physical radius of active particles.

Parameter	Anode (A1)	Cathode (C1)	Cathode (C2)	Cathode (C3)	Cathode (C4)
Composition, (AM/ CB, weight ratio)	91:9	94:6	94:6	94:6	90:10
Thickness, μm	75	75	84	84	72
Density, g/cm^3	1.22	2.56	2.23	2.23	2.09
Porosity, %	45.31	41.42	47.71	47.72	48.10
Active particle size, μm	$X_{10,3} =$ 4.98	$X_{10,3} =$ 2.46	$X_{10,3} =$ 2.46	$X_{10,3} =$ 3.81	$X_{10,3} =$ 2.46
	$X_{50,3} =$ 6.98	$X_{50,3} =$ 3.92	$X_{50,3} =$ 3.92	$X_{50,3} =$ 6.38	$X_{50,3} =$ 3.92
	$X_{90,3} =$ 9.26	$X_{90,3} =$ 5.35	$X_{90,3} =$ 5.35	$X_{90,3} =$ 9.15	$X_{90,3} =$ 5.35

it played an important role in electrochemistry (electronic conductivity), while the effect on pore phases and mechanical properties cannot be ignored.

Generally, the uniformity of the pore after particle rearrangement determines the cell's aging and final output. Considering mass transport limitations and charge transport capacity, the electrodes are densified, and high-energy density is increased at the expense of power performance. In terms of the active material/carbon additive/binder composition and the amount of solvent used during the preparation of the slurries, Primo et al. systematically investigated the effect of calendaring conditions (rolling force and temperature) on the porosity of the $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ -based electrodes [11]. The maximum volume capacity was achieved at moderately applied pressure (60–120 MPa) and temperature (60 °C–75 °C) [12]. When the roll pressure is high, the particles' fragmentation leads to shortened cycle life and reduced capacity [13]. Note the length of the deformation zone of the electrode can affect the transient pressing overload and leads to strip breaking. From a more engineering point of view, Schreiner et al. developed a qualitative machine/material-process-structure model to elaborate the dependencies between individual parameters and process steps [14]. Although previous work made significant contributions to understanding how the calendaring process determines the final LIB performance, further understanding of the evolution of mechanical and microstructure during the calendaring process is needed to guide product design and process production.

This study aims to reveal the evolution mechanism of mechanics and microstructure during the calendaring process, while a predictive model is derived for the determination of the thickness and porosity of the electrode. From a microscale level, the DEM is taken to analyze the calendaring process. The macroscale response, such as the electrode's thickness, porosity, and elastic recovery, was derived by capturing the interaction behavior of the active particles and CB. The simulation results were calibrated and validated by nanoindentation measurements and calendaring experiments, which provides the possibility to characterize other features and gain insight into the calendaring process. A detailed and systematic study of the impact of the line load on the electrode mesostructure, pore size distribution, resistance evolution, and coating-current collector interaction. Furthermore, the compaction machines have high requirements for the control of electrode densification, the prediction model provides relevant theoretical knowledge. Our study provides a reference for the design and manufacturing process of the electrode.

2. Material and methods

2.1. Electrode composition and experimental methods

The cathode and anode electrodes were manufactured and physically characterized to calibrate the contact model (A1, C1). The other three cathode electrodes for analyzing the effect of structural parameters on

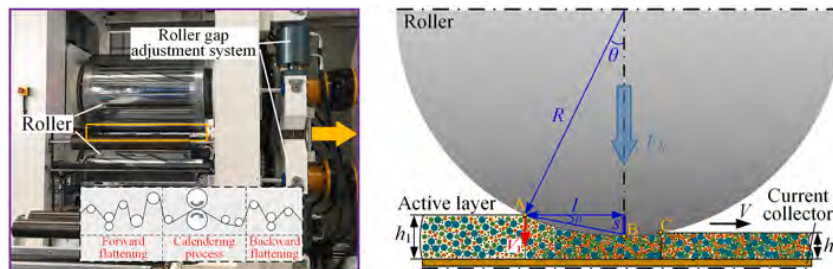


Fig. 1. Electrodes were calendared by a production-scale two rollers compactor. The compactness between active particles increased significantly along the calendaring direction and elastic recovery occurred at the outlet (point B – C).

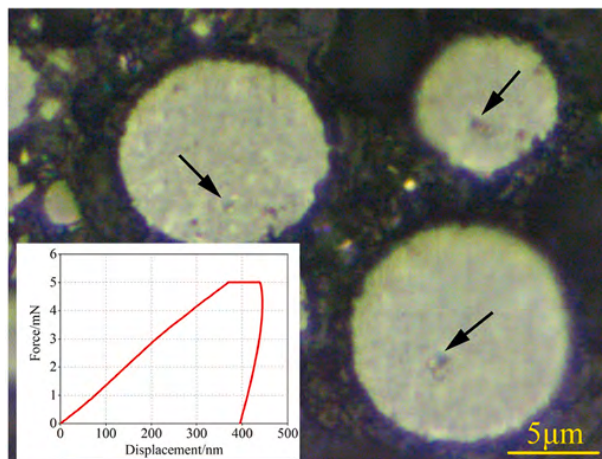


Fig. 2. Nanoindentation on individual particles under optical imaging. The inset figure shows a typical load-unload curve.

the mechanical properties (C2, C3, C3). The relevant structural and characterization parameters of the uncalendered electrodes are shown in Table 1, with coatings on both sides of the current collector. Porosity was measured using a Hg intrusion porosimeter, and scanning electron microscope (SEM) images obtained the active particle size. A production-scale two rollers compactor calendared the electrodes. The roller diameter is 900 mm, the width is 1300 mm, and the calendaring speed is 5 m/min. As depicted in Fig. 1, the single-cylinder of the

calender press controls the gap size and bending force by applying different line loads. The configured machine vision inspection system kept the electrode thickness error within $\pm 2 \mu\text{m}$. The active material of anode is mesocarbon microbeads graphite powder. The active particle of cathode is $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NMC-622). The size of the CB is $2 \mu\text{m}$. Other components were battery grade.

The electrodes were polished using a cross-section polisher (IB-19510 CP), and the SEM images were acquired with a scanning electron microscope (SEM-EDS, FEI). The current collector surfaces were imaged using an atomic force microscope (Baker). Polyvinylidene fluoride (PVDF, binder) for the cathode electrode is chemically stable and dissolves only in a few solvents or at high temperatures [15]. The complete aluminum foil was obtained by immersion in *N*-methylpyrrolidone (NMP) and heating in a water bath at 70°C for 0.5 h, followed by ultrasonic cleaning.

The Young's modulus of particles mainly affects the magnitude of the compressive load on the electrode. Nano-indenter instrument (CPX-NHT 2) was employed to measure the mechanical properties. The uncalendered sample was fixed with epoxy resin, and polished using $0.05 \mu\text{m}$ colloidal silica suspension. Nanoindentation tests were performed using Berkovich triangular pyramid indenter at a constant loading rate of $0.1 \mu\text{m}\cdot\text{min}^{-1}$ and held for 5 s at the peak. As shown in Fig. 2, the center of selected active particles diameter larger than $8 \mu\text{m}$ as targets to avoid the effect of the surrounding medium with reference to the study of Vasconcelos et al. [16]. Considering the difference in particle shape and substrate effects, 30 particles were tested by nanoindentation with an indentation depth of 300 nm. The elastic modulus was obtained following the Oliver–Pharr method [17].

Nanoindentation curves verified the accuracy of the DEM model. Tests were performed using a flat punch indenter with a diameter of 100

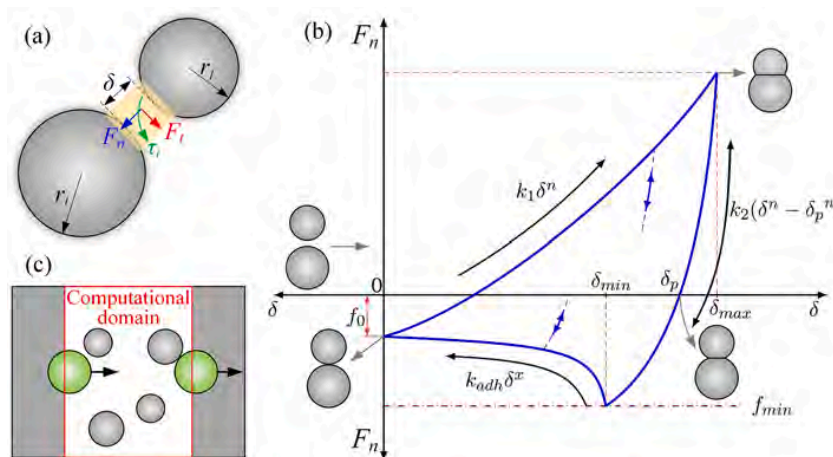


Fig. 3. (a) Interaction between two particles; (b) Generalized form of EEPA model; (c) The linear periodic boundary.

μm (UNHT). Indentation tests were performed at a constant strain rate of $1 \mu\text{m s}^{-1}$, and the maximum indentation depth was below 10% of the electrode thickness to eliminate the effect of the current collector. The electrode thickness mentioned here generally refers to the thickness of the coating on one side. Each sample was measured at non-overlapping locations, and abnormal results with crossover or pop-out curves were discarded [18].

2.2. Discrete element method

DEM is now widely used to deal with engineering problems of dense granular materials, with the advantage that the particles are modeled individually, and no intrinsic model is needed to represent the overall behavior [19,20]. As previously described, the active particles and CB are bonded by a binder network (cohesive bulk), and the compression process of the coating involves particle interaction and elastic-plastic deformation. The kinematic properties of cohesive granular solids strongly depend on the prior consolidation stress [21]. In this work, the Edinburgh Elasto-Plastic Adhesion (EEPA) model [22,23] was used to capture the mechanical response of the electrode. This model is a mesoscopic adhesive contact model. The contact plasticity and stress history dependency in particle contact deformation are illustrated to provide insight into the effect of input parameters on the cohesive bulk behavior [24].

The relationship between particle overlap-force for the EEPA contact model is shown in Fig. 3. The interaction forces of particle extrusion in Fig. 3a are the total contact normal force, F_n , the total applied torque, τ_i , and the contact tangential force, F_t . Meanwhile, the model also considered the increase in adhesion force with increasing plastic contact area. The generalized form of normal force-overlap (F_n - δ) for the EEPA model is shown in Fig. 3b. The loading, unloading and adhesive branches are represented by the virgin loading stiffness k_1 , the unloading stiffness k_2 , and the adhesive stiffness k_{adh} . k_1 and k_2 provide elasto-plastic contact. The exponent n determines its nonlinearity. When $n = 1$, the model is a linear spring model, and when $n = 1.5$ (in this paper), it will replicate the Hertzian spring model.

The total contact normal force is the sum of the hysteretic spring force and the normal damping force:

$$F_n = (F_{hys} + F_{nd})\mathbf{u} \quad (1)$$

where $\mathbf{u}$ is the unit normal vector in the direction of the contact particle center line. The force-overlap relationship for normal contact, F_{hys} , is mathematically expressed by Eq. (2).

$$F_{hys} = \begin{cases} f_0 + k_1 \delta^n & \text{if } k_2(\delta^n - \delta_p^n) \geq k_1 \delta^n \\ f_0 + k_2(\delta^n - \delta_p^n) & \text{if } k_1 \delta^n > k_2(\delta^n - \delta_p^n) \\ f_0 - k_{adh} \delta^n & \text{if } -k_{adh} \delta^n \geq k_2(\delta^n - \delta_p^n) \end{cases} \quad (2)$$

The loading stiffness k_1 is as follows:

$$k_1 = \begin{cases} 2E^* R^* & n = 1 \\ \frac{4}{3} \sqrt{R^* E^*} & n > 1 \end{cases} \quad (3)$$

where E^* is the equivalent Young's modulus, R^* is the equivalent radius.

During the loading/unloading process, the particle deformation and elastic recovery depend largely on contact plasticity. This paper, it is described by the contact plasticity ratio λ_p .

$$\lambda_p = \left(1 - \frac{k_1}{k_2}\right) = \frac{\delta_p}{\delta_{max}} \quad (4)$$

where δ_p is the residual overlap between particles, δ_{max} is the maximum overlap between particles. If the values of k_1 and k_2 are equal, the model is elastic.

The normal damping force, F_{nd} , is given by:

$$F_{nd} = -\beta_n \mathbf{v}_n \quad (5)$$

where $\mathbf{v}_n$ is the magnitude of the relative normal velocity, and the normal damping coefficient β_n is defined as:

$$\beta_n = \sqrt{\frac{4m^* k_1}{1 + (\pi/ln e)^2}} \quad (6)$$

where m^* is equivalent mass, e is the coefficient of restitution.

The contact tangential force, F_t , is given by the sum of tangential spring force, F_{ts} , and tangential damping force, F_{td} :

$$\mathbf{F}_t = \mathbf{F}_{ts} + \mathbf{F}_{td} \quad (7)$$

The tangential spring force is calculated by:

$$\mathbf{F}_{ts} = \mathbf{F}_{ts(n-1)} + \Delta \mathbf{F}_{ts} \quad (8)$$

where $\mathbf{F}_{ts(n-1)}$ is the force of the previous time step, and the incremental tangential force $\Delta \mathbf{F}_{ts}$ is calculated by:

$$\Delta \mathbf{F}_{ts} = -k_t \mathbf{v}_t \Delta t \quad (9)$$

where k_t is the tangential stiffness, $\mathbf{v}_t$ is the magnitude of the relative tangential velocity, Δt is the time step. The tangential stiffness can be calculated by:

$$k_t = \zeta_{tm} \begin{cases} k_1 & n = 1 \\ 8G^* \sqrt{R^* \delta_n} & n > 1 \end{cases} \quad (10)$$

where ζ_{tm} is the tangential stiffness multiplier, G^* is the equivalent shear modulus. The tangential damping force F_{td} is calculated by:

$$\mathbf{F}_{td} = -\beta_t \mathbf{v}_t \quad (11)$$

The tangential damping coefficient β_t is defined as:

$$\beta_t = \sqrt{\frac{4m^* k_t}{1 + (\pi/ln e)^2}} \quad (12)$$

The generation of the coating and calendering process was completed by Altair® EDEM™ software, which can visualize the simulation and the statistics in real time for bulk and granular material. This study adopted the standard rolling friction for the torque calculation. For simulations in which rolling friction is important, this is accounted for by applying torque to the contacting surfaces. The total applied torque, τ_i , is calculated as follows:

$$\tau_i = -\mu_r |F_{hys}| R_i \omega_i \quad (13)$$

with μ_r the coefficient of rolling friction, R_i the distance of the contact point from the center of mass, and ω_i the unit angular velocity vector of the object at the contact point.

For the description of sliding friction, the critical sliding friction F_{ct} is calculated using the Coulomb friction criterion:

$$F_{ct} \leq \mu |F_{hys} + k_{adh} \delta^n - f_0| \quad (14)$$

where μ is the friction parameter.

The adhesive force is related to the plastic contact overlap and the surface energy. The particle surface will flatten at the contact point, and the amount of flattening depends on the applied load. The contact radius, r , is given by Eq. (15):

$$r = \frac{1}{2d} \sqrt{4d^2 r_i^2 - (d^2 - r_j^2 + r_i^2)} \quad (15)$$

where d is the distance between the two centers of mass, r_i , r_j are the radius of the two contacting particles.

All particles are embedded in the binder to form a complete physical

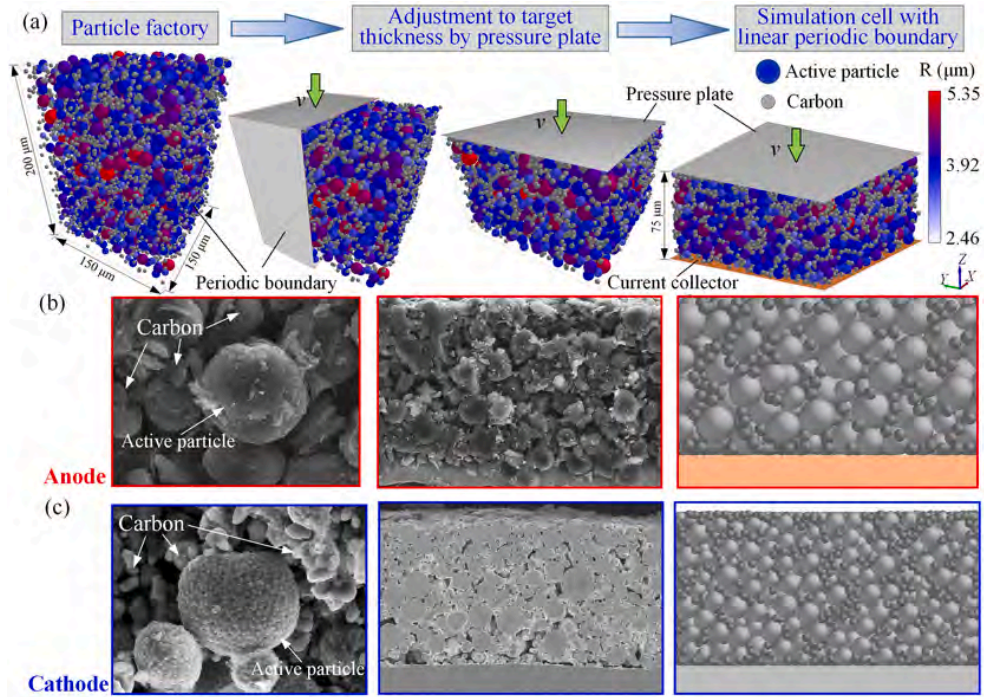


Fig. 4. (a) Details of the model generation with electrode C1 as an example; (b) SEM image of the particle morphology (left), the manufactured electrodes A1 (middle), the numerically generated structure (right); (c) SEM image of the particle morphology (left), the manufactured electrodes C1 (middle), the numerically generated structure (right).

structure while bonded to the current collector. This provides a conductive network for electron transport and ensures the integrity of the electrodes [25]. Thus, the adhesive force of particle-particle interactions is determined by setting the surface energy. The minimum adhesive force f_{min} is now determined from the product of the plastic contact overlap and the surface energy of the contact. Once the contact force reaches the limiting value f_{min} , separation of the contact can occur. The Hertz-Mindlin model was used for the particle-geometry contact.

In the software, only Poisson's Ratio, ν , and Young's modulus, E , were set as input parameters with the shear modulus, G , calculated from these as required.

The equivalent Young's modulus E^* is defined as:

$$\frac{1}{E^*} = \frac{(1 - \nu_i^2)}{r_i} + \frac{(1 - \nu_j^2)}{r_j} \quad (16)$$

The equivalent shear modulus G^* is defined as:

$$\frac{1}{G^*} = \frac{(2 - \nu_i)}{r_i} + \frac{(2 - \nu_j)}{r_j} \quad (17)$$

Moreover, the equivalent radius R^* is defined as:

$$R^* = \frac{r_i \times r_j}{r_i + r_j} \quad (18)$$

The equivalent mass m^* is defined as:

$$m^* = \frac{m_i \times m_j}{m_i + m_j} \quad (19)$$

where m_i and m_j are the masses of the two particles in contact.

2.3. Generation of particle electrode structures

The model domain is the area where simulation takes place. The box

in the environment section defines it. Domain size has an effect on simulation time; the larger the domain, the longer the simulation will take to run. In this work, the model domain size is set to $150 \times 150 \times 200 \mu\text{m}$, consistent with the particle factory. The circumferential linear periodic boundary in the X and Y direction is opened (particle motion is restricted in the Z-direction), as shown in Fig. 4a. Any particle leaving the domain in that direction will instantly re-enter it on the opposite side and interacts with material on the opposite side of a boundary. As shown in Fig. 3c, the particle on the left will be visualized as a whole on the left side of the screen until its center point passes the boundary; however, the particle will still contact material on the other side of the boundary.

The top of the computational domain is a movable pressure plate with the material property set to steel. The bottom is a current collector with the material property set to copper (anode) and aluminum (cathode). Fig. 4a presents the details of the model generation with electrode C1 as an example. Dynamic factories are used to generate particles. The total masses of active particles and CB are first calculated and generated in the domain at a rate of 10^{-4} kg/s . The position of particle generation is random. After reaching the target mass, the plate moves downward to compress the coating until it reaches the target thickness of the unlendered electrode. Subsequently, the calendaring simulation will be carried out on the simulation cell with linear periodic boundary. Fig. 4b and Fig. 4c show the cross-section SEM images of cathode and anode electrodes with the morphology of the simulated structure. Considering the limitation of particle size on the calculation, the fixed time step was set to 10^{-10} s .

3. Results and discussion

3.1. Model calibration and mechanical characterization

Nanoindentation is a common method used to characterize the materials' mechanical properties. The mechanical work performed by

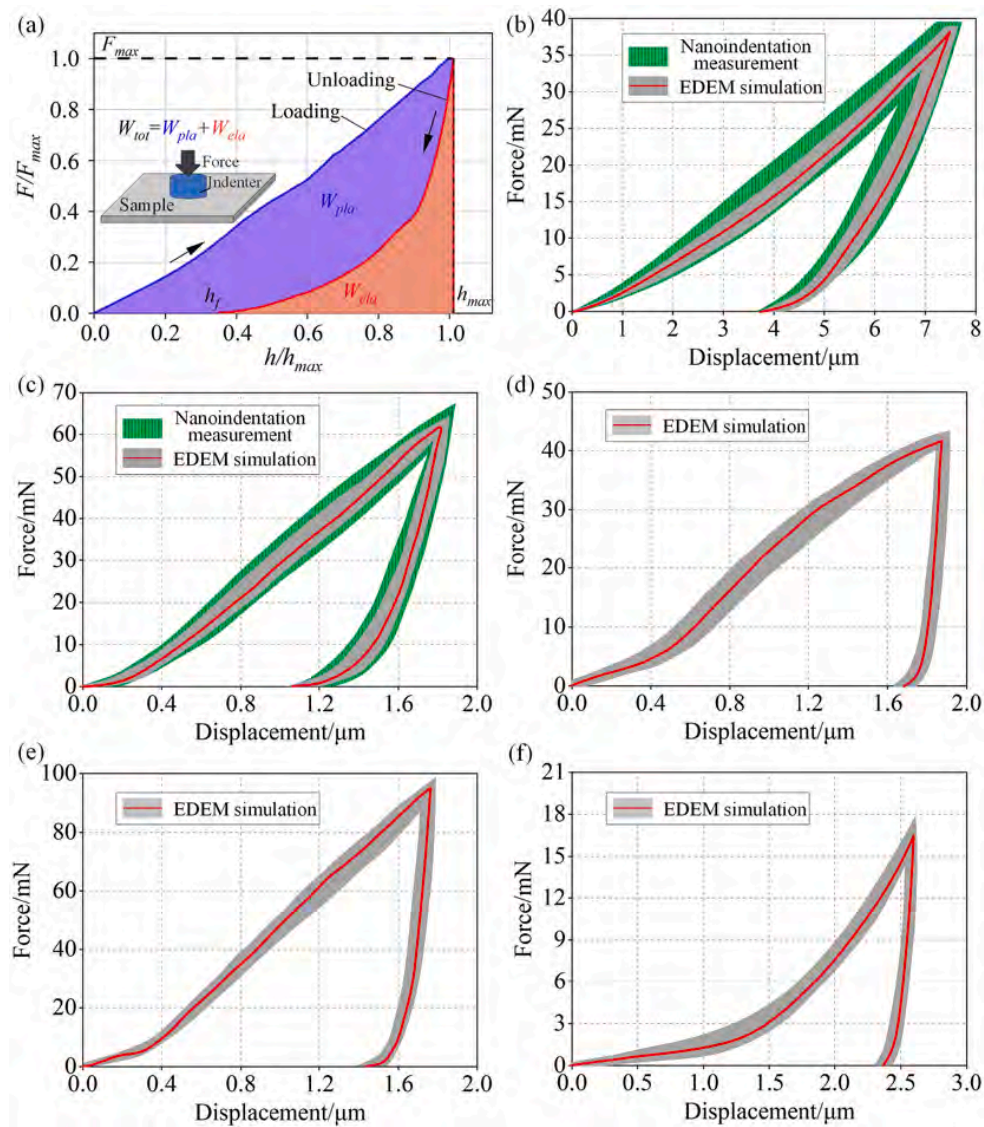


Fig. 5. (a) Schematic view of the force-displacement curve and calculation of the indentation work (η_{it}); (b) Electrode A1; (c) Electrode C1; (d) Electrode C2; (e) Electrode C3; (f) Electrode C4. Green region represents experimental results and gray region represents simulation results. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

indentation is defined as W_{total} , which is given by the sum of the plastic deformation (W_{pl} , blue area in Fig. 5a) and the elastic deformation (W_{el} , red area in Fig. 5a) as shown in Eq. (20) according to Ni et al. [26].

$$W_{total} = W_{pl} + W_{el} = \int F_{load} dh \quad (20)$$

$$W_{el} = \int F_{unload} dh$$

where F_{load} and F_{unload} are test forces during loading and unloading respectively, dh the corresponding indentation depth. The indentation work η_{it} is shown in Eq. (21), which can be used to compare the elasticity of electrode samples. The greater the indentation work, the smaller the elasticity.

Table 2
Input parameters for the characterization of particles.

Parameter	Anode	Cathode
Particle density, ρ	2.2 g·cm ⁻³	4.74 g·cm ⁻³
Young's modulus, E	0.76 GPa	75 GPa
Poisson ratio, ν	0.3	0.25
Coefficient of restitution, e	0.25	0.25
Contact plasticity ratio, λ_p	0.8	0.96
Constant pull-off force, f_0	10 ⁻⁵ N	10 ⁻⁵ N
Rolling friction coefficient, μ_r	0.01	0.012
Sliding friction coefficient, μ	0.1	0.12
Surface energy (AM-AM)	15 J·m ⁻²	8 J·m ⁻²
Surface energy (AM-CB)	30 J·m ⁻²	20 J·m ⁻²
Surface energy (CB-CB)	80 J·m ⁻²	60 J·m ⁻²

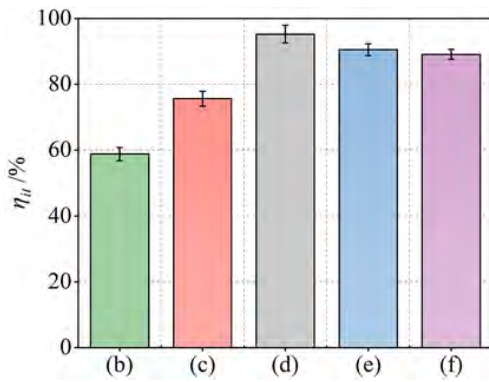


Fig. 6. Indentation work corresponds to the sample in Fig. 5.

$$\eta_{ii} = \frac{W_{plast}}{W_{total}} (\%) \quad (21)$$

Table 2 lists the parameters needed for simulation. In addition to measuring parameters, two parameters need to be revised reversely by comparing the simulation and experiment load-displacement curves. The change of surface energy mainly determines the slope of the loading curve, the maximum compressive load is mainly determined by particle Young's modulus, and the unloading curve is determined by the contact plasticity ratio [27]. Considering that the randomness of particle position generation can make a difference in results, all simulations were run five times with different stochastic initial packings. Likewise, 20 measurements were performed at different locations of the A1 and C1 samples and compared with the simulated results.

Fig. 5 shows that the simulation results of load-displacement curves agree well with the experimental, and the calculated values of the indentation work are given in Fig. 6. It can be seen that the anode electrode presents a large elastic recovery due to the small contact plasticity ratio and Young's modulus of active particles. Hence, the graphite anode electrode needs to be continuously calendered twice in industrial production to make the pore phases uniformly distributed over the entire electrode [28]. On the contrary, the anode electrode

presents more resistance to compaction. The particle contacts number and the maximum compaction load decrease due to the increase in pore and CB content. However, the increase in active particle size leads to an increase in the maximum load, with fewer contacts for larger active particles, resulting in a straightforward transmission of the force to the current collector. Therefore, the calibrated model and the comparison variable parameters can capture the effect of material structure changes on the mechanical properties and elastic-plastic behavior.

3.2. Mechanical and microstructural evolution

LIB electrode is essentially a porous composite material with a three-layer structure. To visualize the evolution of electrode structure during calendering, a sample from the deformation zone was obtained at a 28.3% reduction rate for the cathode electrode C1 as an example, and the results are shown in Fig. 7. The aluminum foil thickness is 15 μm. It can be seen that the compactness of the coating increases significantly as the calendering process, and the current collector as a whole is not thinned. The cross-sectional polishing of the four positions corresponding to the inlet to the outlet was performed to analyze the morphological evolution of the deformation zone.

Near the roller gap inlet, the coating collapses at position (a), active particles move and rotate, and CB redistributes in the pores. In this process, the porosity decreases, and the coating is separated from the current collector. With further compression, at position (b), the distance between particles decreases, and due to the friction, the pressure gradually increases. At position (c), elastic-plastic deformation occurs after particles contact extrusion and the compressive force increases significantly. At position (d), there is an elastic recovery of the electrode, but the reaction force of elastic recovery on the rollers can be ignored. The side morphology of the current collector shows that the overall thinning does not occur, and some particles at the outlet will be embedded in the surface. In order to ensure the safety of battery operation, it is not expected that the current collector will deform.

The pressure within the deformation zone is difficult to measure experimentally. Zhang et al. et al. simplified the coating compression as a plane deformation, divided the deformation zone into several micro-elements, and established a calculation model for pressure distribution and rolling force in the deformation zone [29]. In this work, the DEM

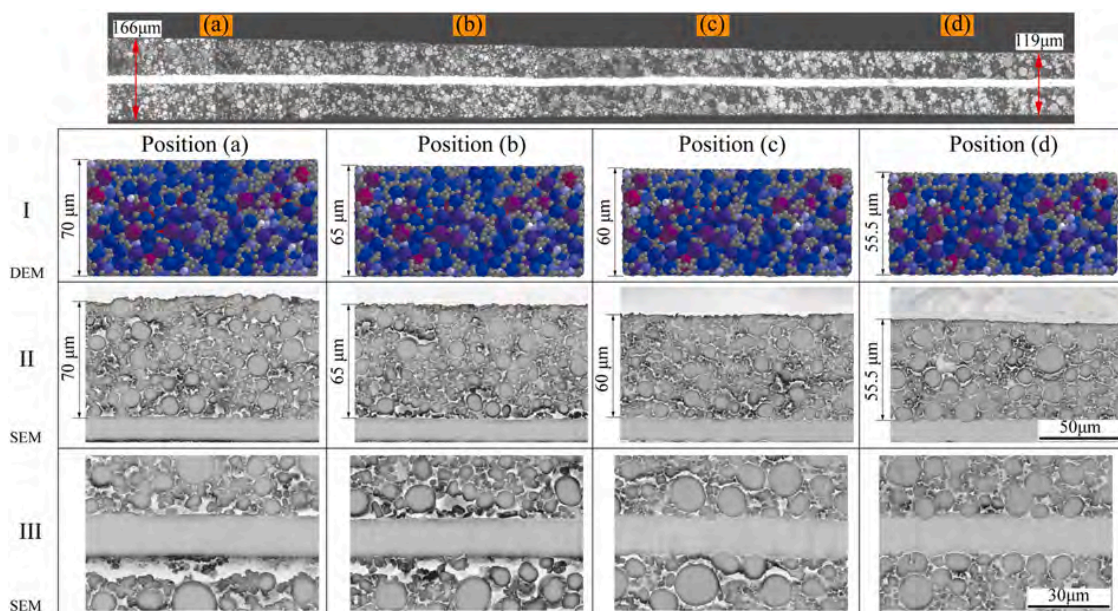


Fig. 7. Deformation zone cross-section SEM images of cathode electrode C1. Comparison of DEM simulation results (I) and SEM images (II, III) after calendering.

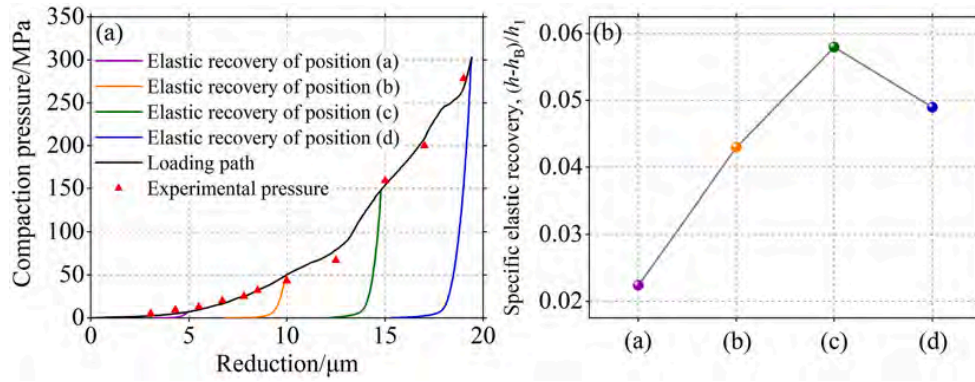


Fig. 8. (a) Evolution of unit pressure with reduction for the calendared electrodes, the reduction is 5 μm , 10 μm , 15 μm , 19.5 μm respectively corresponding to Fig. 7; (b) Elastic recovery rate at different reductions, h is the final thickness of the electrode, h_B is the roller gap thickness, h_1 is the initial thickness of the electrode.

was used to investigate the mechanical and microstructural evolution based on the preliminary analysis of the structural evolution within deformation zone. The simulation time of the complete calendaring process was long, so a representative volume element (RVE) was sufficient to assure valid and representative results, as shown in Fig. 7 (I). Take the cathode electrode C1 of $150 \times 150 \times h_1 \mu\text{m}$ as the object (h_1 is the original thickness of electrode, as shown in Fig. 1). The active particle number is 1966, and the CB number is 4502. The total number of particles, C_{tot} , is 6468. The coordination number [30], CN , can be calculated by $CN = C_p/C_{tot}$. The contact between electrode and roller surface is mainly in the normal direction due to the different order of magnitude between the particles and roller. As can be seen from the schematic in Fig. 1, the contact angle θ between the roller and the electrode is calculated as:

$$\theta = \cos^{-1} \left[\frac{R - (h_A - h_B)}{R} \right]$$

Due to the clear contrast between the roller radius (450 mm) and the electrode thickness, θ is less than 1° in all cases. The contact angle is 0.98° when the electrode thickness after calendaring is 100 μm . Taking this into account, any small area in the deformation zone can be considered as compression in the thickness direction. In addition, the component of the calendaring velocity in the thickness direction is maximum at position A and becomes zero at position B. The velocity component at position A is very low, even if it remains constant throughout equal to the velocity at position A, the kinetic energy changes insignificantly [10]. Hence, the plate moved downward with the entrance velocity V_1 pressed down. From position B to C, the velocity moving upwards is at the same speed but in the opposite direction.

The loading-unloading curves and elastic recovery rates of the elements are given in Fig. 8. The simulation of the loading curve agrees well with the experimental results, and the model's thickness, porosity, and rolling force will also be verified in Section 3.5. It can be seen that the compression pressure increases slowly at the beginning due to the pore

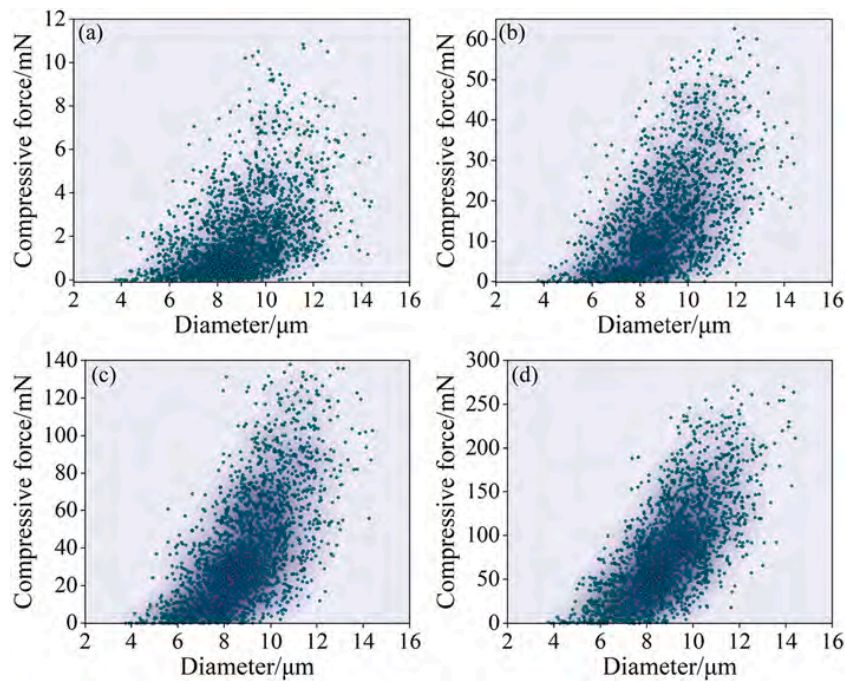


Fig. 9. Compressive pressure of the active particles within electrode C1. Reduction: (a) 5 μm , (b) 10 μm , (c) 15 μm , (d) 19.5 μm .

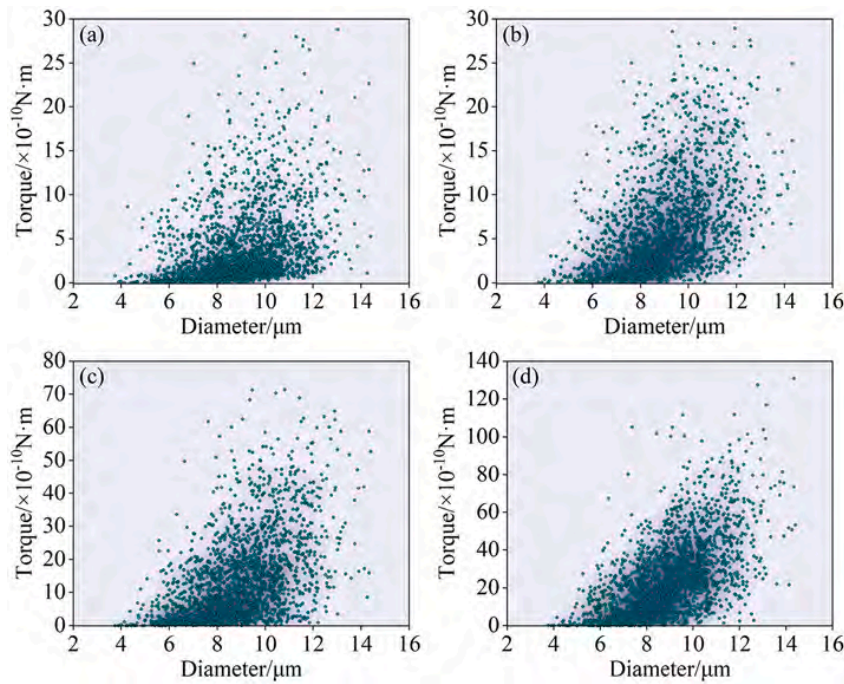


Fig. 10. Total torque of the active particles within electrode C1. Reduction: (a) 5 μm , (b) 10 μm , (c) 15 μm , (d) 19.5 μm .

reduction and particle rearrangement after the compression. In this sense, the electrode exhibits low stability at low loads. The compression pressure increases exponentially as the friction and mutual extrusion between the particles. After removing the pressure, the electrode elastic recovery is shown in Fig. 8b. It can be seen that the elastic recovery increases first and then decreases. This is because the initial compression stage is mainly the deformation of the PVDF network and the reduction of porosity. Then the elastic recovery increases until the particles are deformed plastically. But when most particles exceed the yield point, the elastic recovery will decrease. It is conceivable that when the electrode reaches its minimum thickness, the particle will deform plastically or even ruptured, and the elastic recovery at this point will become zero.

From the above analysis, it is clear that interparticle friction and extrusion are the main factors hindering compression deformation. Considering the small size and small deformation resistance of CB, the evolution of compressive force and torque of the active particles are given quantitatively in Fig. 9 and Fig. 10, respectively. However, from the point of view of data size, it is difficult to determine which impact is more important in the compression process. It can be inferred from the structural evolution of the deformation zone in Fig. 7 that the friction at the initial stage has a greater hindrance to compression. The compressive force is about 250 mN, and the torque is about $100 \times 10^{-10} \text{ N}\cdot\text{m}$ when the press quantity is 19.5 μm , mainly for particles with larger particle sizes.

3.3. Stress tensor analysis

Basic scalar parameters such as porosity and particle forces often cannot reflect the information about the directionality of the contact between the particles within the coating. The close particle contact after calendaring forms a more complex contact force network and requires vectors to describe in detail the distribution of the contact force network in each direction. In this work, the stress tensor σ_{ij} within the simulation cell is used to describe:

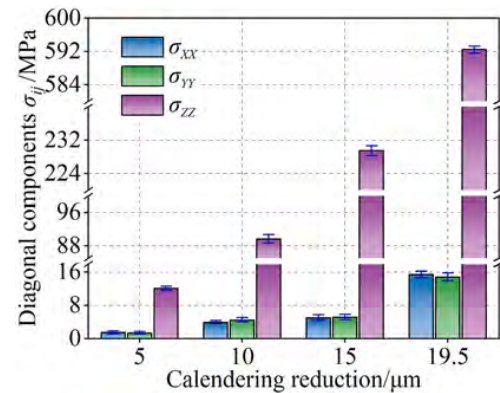


Fig. 11. Diagonal components of the stress tensor σ_{ij} for the calendared electrodes under different reduction.

$$\sigma_{ij} = \frac{1}{2V} \sum_i (r_{1i} F_{1j} + r_{2i} F_{2j}) \quad (22)$$

where r_{1i} and r_{2i} are the relative positions of the two interacting particles, F_{1j} and F_{2j} are the interacting forces. Therefore, the diagonal of each single particle stress tensor is summed, and the total macroscopic stress was averaged over the total volume V of the simulation cell. Fig. 11 shows the calculated results for the diagonal components. The stresses inside the coating both increase as the number of reduction increases. σ_{xx} and σ_{yy} are approximately the same and lower, and σ_{zz} in the normal direction is higher for all calendaring conditions. This evolution pattern is related to the directionality of the interparticle contact stresses, so the stress tensor can reflect the anisotropic characteristics of the internal contact of the coating [31]. Considering different directions, it is likely to affect the cell's capacity decay and final failure. The anisotropic structure increases the curvature of the electrode thickness

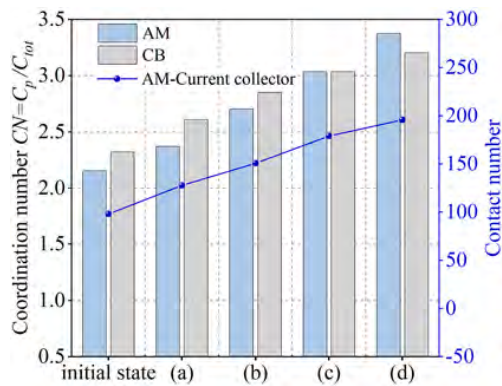


Fig. 12. Coordination number of AM, CB, and contact number of AM-Current collector. Reduction: (a) 5 μm, (b) 10 μm, (c) 15 μm, (d) 19.5 μm.

direction, which can have a negative impact on the cell operation.

3.4. Electronic conductivity

Furthermore, the total contact surface area of active particles and CB is also considered one of the most important characteristics in determining the pressure required for electrode densification. A larger free surface area allows for maintaining a smaller local overpotential at higher charging and discharging rates, thus reducing activation losses while reducing the resistance to charge transfer [32]. This will affect the electronic conductivity of the electrode. In the case of increasing electrode density, the electron conductivity and ionic conductivity change oppositely. On the one hand, the conductive path inside the electrode is improved, that is, the number of contacts between particles increases, but the progressively sealed percolation paths reduce the ionic conductivity. On the other hand, the contact between the coating and the

current collector is tightened. This can be explained by the coordination number between the active particle, CB, and the number of contacts between the active particle and the current collector, as shown in Fig. 12. Meanwhile, the resistance and resistivity of the electrode were measured by a planar-controlled voltage probe. Using Kelvin's four-wire method and alternating current excitation current, the indenter material is copper, which can adjust the test pressure and measure the thickness. The results are shown in Fig. 13. With the increased compaction pressure, the electric resistance does not always decrease. The resistance remains almost unchanged after 30 MPa, about 0.31 Ω. It can be seen from Fig. 13b that active particles and CB are embedded in the PVDF network, and CB mainly contributes to the conductivity. However, the few proportions of CB, and the effect of further densification of conductive network on establishing a new conductive path is weakened. Fig. 13c shows the average contacting neighbours of CB at different electrode thicknesses. As the thickness decreases, the average contact number increases and finally the increase rate slows down. In addition, from the experimental point of view, position (a) in Fig. 7, in the initial state, the coating is separated from the current collector, and the better contact between the two after loading is the main reason for the sharp decrease of the electric resistance.

3.5. Process modeling and deformation mechanism

Based on the Heckel equation for powder compression, a calculated relationship between pressure and porosity can be established. Recently it has been used to analyze the calendaring process of the electrode [2]. The relationship between the line load and the porosity is expressed in Eq. (23).

$$\varepsilon = \varepsilon_{\min} + (\varepsilon_0 - \varepsilon_{\min}) \exp(-q_L/\gamma) \quad (23)$$

where ε_0 and $\varepsilon_{\min}$ are the initial and minimum porosity, respectively. γ is the compaction resistance of the coating, a parameter characterizing the compaction behavior. q_L is the line load, and the unit is $\text{N}\cdot\text{mm}^{-1}$.

However, simply relating the line load to porosity is not sufficient for

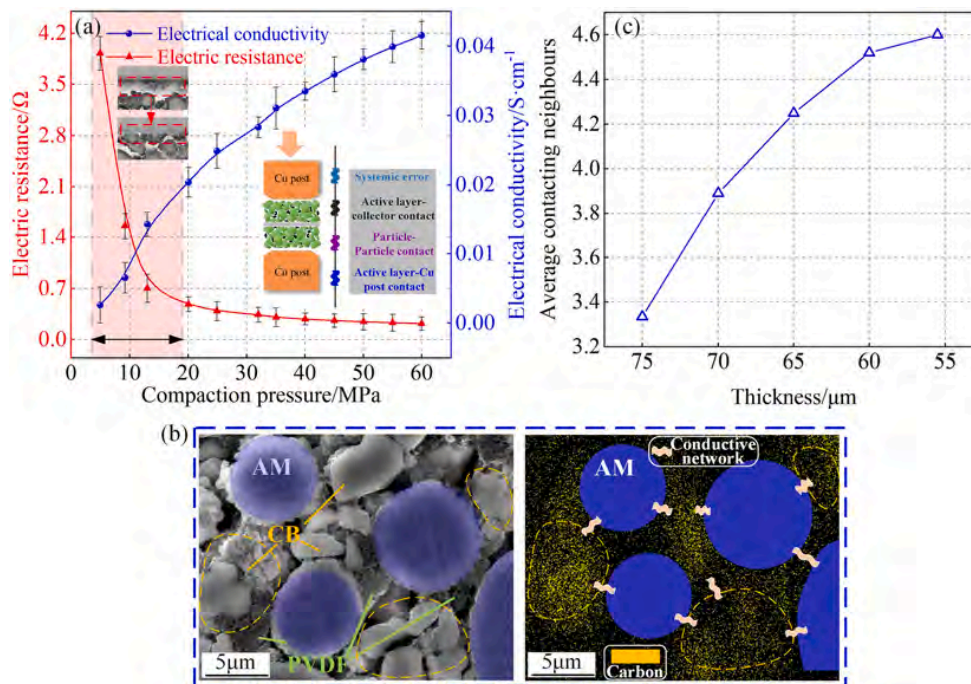


Fig. 13. (a) Experimental results of the electrode electric resistance and electrical conductivity changing with compaction pressure. The inset figure shows the source of error in the test process; (b) The distribution of elemental carbon and conductive network; (c) The average contacting neighbours of CB.

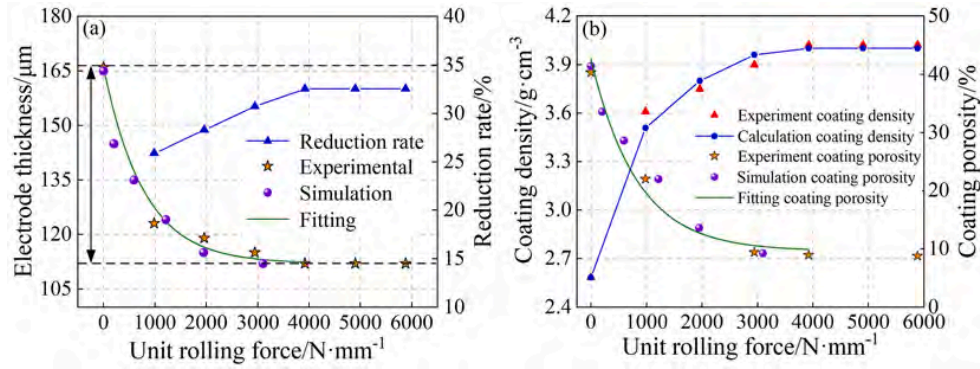


Fig. 14. Relevant experimental, simulation, and fitting results. (a) Evolution of the electrode thickness and reduction rate; (b) Evolution of the coating density and porosity.

the full application of the Heckel equation. In this work, a computational model to predict the density and porosity by measuring the electrode thickness was developed, and the accuracy of the DEM simulation results was examined. Related experiments, simulations, and fitting results are shown in Fig. 14. Using representative volume element (RVE) in the DEM model to calculate line load can be expressed as Eq. (24). The deformation zone of the electrode was divided into s elements with equal width, and the line load can be calculated by cumulative summation. The deformation force of the current collector was not considered here.

$$q_L = \sum_{i=1}^{i=s} \frac{F_i l}{a^2 s} \quad (24)$$

$$l = \sqrt{R^2 - [R - (h_1 - h)]^2}$$

where l is the length of the deformation zone (section AB in Fig. 1), F_i is the compressive force of the RVE, and a is the side length of the RVE (both 150 μm). R is the roller radius, B is the coating width, h_1 is the inlet thickness of the coating, and h is the outlet thickness of the coating.

Rewrite Eq. (23) as follows

$$h = h_{min} + (h_1 - h_{min}) \exp(-q_L/\gamma) \quad (25)$$

where h represents the calculated thickness. The experimental results of the line load and the total thickness were fitted, and the results are shown in Fig. 14a. It is in good agreement with the results of the simulation ($s = 5$) and experiment. Among them, γ is related to the basic properties of material and reflects the difference in the compaction properties of the coating. Here $\gamma = 800$. Bringing $\gamma = 800$ into Eq. (23) to calculate the porosity, the results are shown in the fitted curve in Fig. 14b, which agrees well with the results of the simulation and experiment. Therefore, the total thickness of the electrode is related to the porosity as in Eq. (26), and there is a linear relationship between them:

$$\varepsilon = \varepsilon_{min} + (\varepsilon_0 - \varepsilon_{min}) \left(\frac{h - h_{min}}{h_1 - h_{min}} \right) \quad (26)$$

The coating density ρ is calculated by Eq. (27). The coating porosity can be calculated from the density ρ and the mean physical density ρ_{md} of the components by Eq. (28).

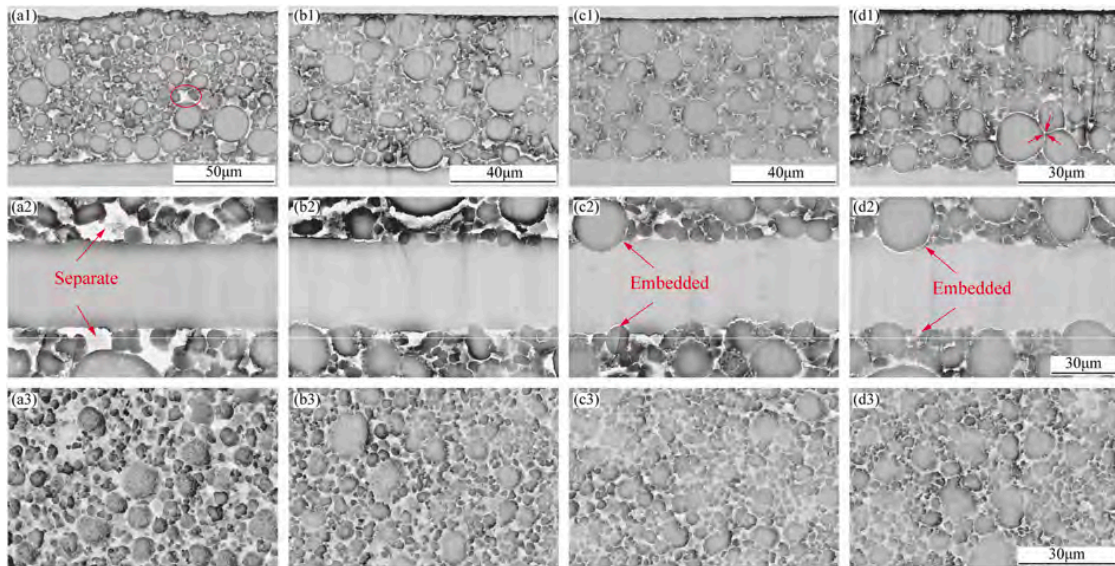


Fig. 15. Cross-section SEM images of electrode calendered to various electrode porosities. (a1-a3) Uncalendered; (b1-b3) 25.9% reduction, 980.39 N/mm; (c1-c3) 28.3% reduction, 1960.78 N/mm; (d1-d3) 32.53% reduction, 4901.96 N/mm.

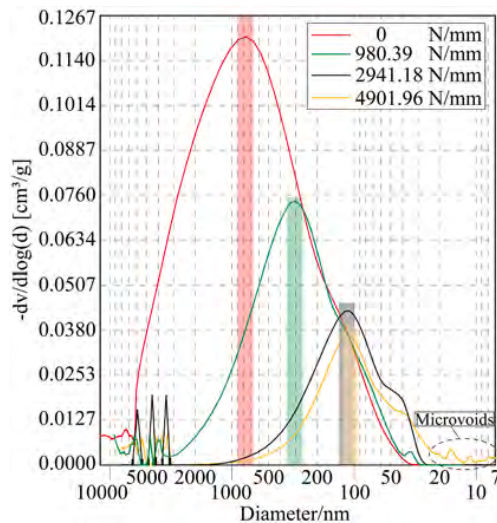


Fig. 16. Pore size distribution of the produced electrodes.

$$\rho = \frac{m - m_c}{H - h_c} \quad (27)$$

$$\varepsilon = 1 - \frac{\rho}{\rho_{md}} \quad (28)$$

where m is the mass loading of the electrode, m_c is the mass loading of the current collector, H is the total thickness of the electrode, and h_c is the current collector thickness, all obtained experimentally. Therefore, the relationship between coating density and line load can be expressed by Eq. (28).

$$\rho = \frac{m - m_c}{(h_{min} - h_c) + (h_1 - h_{min}) \exp(-q_L/\gamma)} \quad (29)$$

The compaction resistance γ calculated above is introduced into Eq. (29), and the fitting results of density are in good agreement with the experimental, as shown in Fig. 14b. When the AM is selected, the compaction resistance γ is calculated by measuring the electrode thickness and the line load, and then the density and porosity are predicted. Therefore, the model equally applies to the prediction of density under other conditions. Among them, the errors in the fitting of compaction resistance, weighing, and thickness measurement of the electrode have a certain influence on the prediction accuracy.

The cross-section SEM images of electrode C1 with different reductions obtained by increasing the line load are shown in Fig. 15. Fig. 15 (a1-a3) shows the original morphology of the electrode C1 with a loose coating structure and intact particles, indicating that slurry preparation does not compromise the particle morphology. At the reduction of 25.9%, the particle spacing in Fig. 15 (b1) decreases, and the carbon-PVDF is compressed. As the reduction increases, these voids serve to intensify stresses at crack tips when particles are compressed during calendaring and differences in fracture strength between the particles. Extrusion exceeds the load limit, and particle flattening or even crushing into multiple particles can be observed. The calendared surface morphology of the electrodes is shown in Fig. 15 (a3-d3). The uncalendared electrode has obvious surface roughness and many uniformly distributed pores, which gradually flatten out with the reduction increase.

The pore size distribution for different line loads, determined by mercury intrusion (Hg porosimetry), is given in Fig. 16. With the increase of line load, the pore size distribution curve is compressed and moved to smaller pores, which means that the coating contains smaller pores and the density increases. And the pore size distribution range

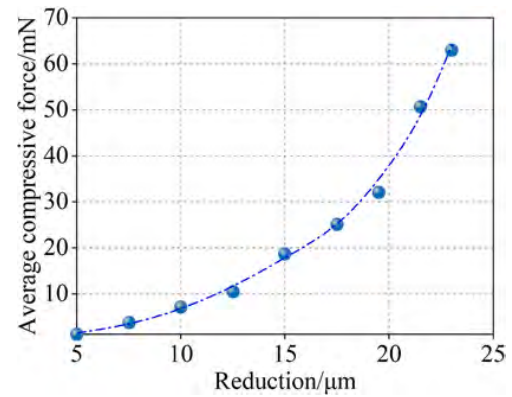


Fig. 17. Simulation results of average compressive force between active particles and current collector.

becomes narrower. This indicates a more uniform pore distribution at higher density, because the pore size distribution is in a smaller range. In addition, when the line load is 4901.96 N/mm, this point exceeds the load limit of most particles, resulting in fracture, so there are microvoids less than 20 nm.

The current collector plays the role of carrying coating and exports the electrons generated by the electrochemical reaction to the external circuit. Therefore, the interaction between the coating and the current collector cannot be neglected. The simulation results of the average compressive pressure between the active particles to the current collector are extracted and shown in Fig. 17. The average compressive pressure increases with the increase of reduction. The Al foil current collectors with a thickness in the range of 10–20 μm have estimated yield strength of around 7 MPa and tensile strength of around 25 MPa at room temperature [33]. Fig. 7 and Fig. 15 show that at a higher line load, particles will embed into the surface to make the aluminum foil deform slightly. This may be related to the broken banding of the electrode that often occurs in the production process. Fig. 18 shows the 3D morphology and height of the current collector surface. The surface of uncalendared aluminum foil is flat. With the increase of the line load, active particles are embedded in the surface, resulting in bulges around. The number of pits on the surface increases, and the deformation is serious. At a line load of 980 N/mm, the embedding depth is within 1 μm . At the minimum thickness of the electrode, the line load is 3921 N/mm, the coating fully contacts with the current collector, and the embedding depth is within 2 μm . In addition, it can be seen from Table 3 that the surface roughness and surface fluctuation increase with the increase of line load. According to the previous research, the surface roughness of the current collector significantly affects the LIB's chemical performance. The rough surface increases the contact area between the coating and the current collector, which improves the electrical conductivity as previously described. On the other hand, the rough surface has good wettability, which facilitates the adhesion between the coating and the current collector, and improves the electrode cycling performance.

Based on the characterization of morphology and structure. Fig. 19 summarizes the deformation mechanism during the calendaring process: particle pulverization, secondary particle fusion, PVDF network compression, and the surface deformation of the current collector. Particle pulverization is observed to various degrees depending on the calendaring level, resulting in free primary particles exposed to the electrolyte and a higher specific surface area. Therefore, it is assumed that the increase in water sorption with increasing density is due to more particle pulverization. These cracks lead to a larger surface area, which enables higher water adsorption after compression [34]. Particles with internal defects are subjected to an increase in local stress after

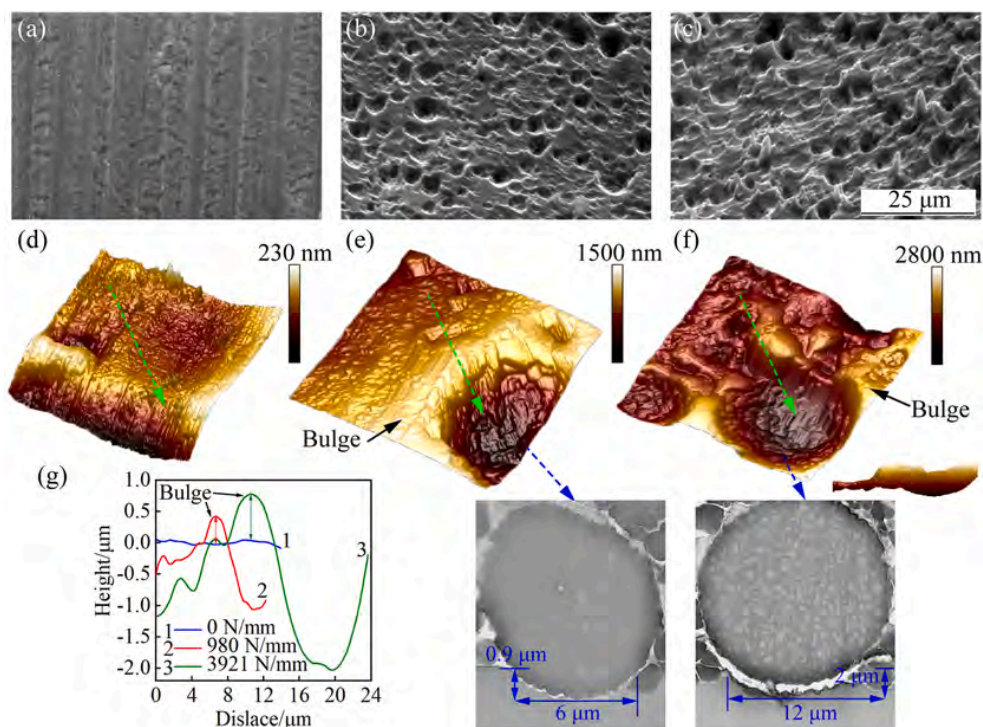


Fig. 18. SEM images of the current collector surface: (a) Uncalendered; (b) 980 N/mm, 25.9% reduction; (c) 3921.6 N/mm, 32.53% reduction; AFM images of the current collector surface: (d) Uncalendered; (e) 980 N/mm, 25.9% reduction; (f) 3921.6 N/mm, 32.53% reduction; (g) Surface fluctuation.

Table 3

Surface roughness of the current collectors.

Line load, N·mm ⁻¹	0	980	3921
Roughness Ra, nm	50	343	762
Surface fluctuation, μm	0.0041	1.48	2.81

compression, resulting in internal crack expansion, as in Fig. 19a. And the fracture strength of particles with large particle sizes is greater. When the pressure at the interface of the two particles is high enough, fusion into secondary particles begins at the contact surface. This means there is no obvious physical gap at the contact boundary, and micro-porous connections achieve the fusion. This makes it difficult for the electrolyte to penetrate sufficiently into the fusion, and its wettability is reduced, limiting ion transport. There are even closed pores, as shown in Fig. 19b. In addition, the particles are not randomly dispersed after breaking but form agglomerates.

4. Conclusions

To investigate the calendering process directly from a microscale level, this paper developed a DEM simulation model based on the EEPA model. Characterization was used to determine the physical characteristics of each individual particle, and nanoindentation measurements were used to calibrate and validate the model. The effects of anode and cathode electrodes, particle size, and AM proportion on micro-mechanical properties were compared. Large particles and the cathode electrode are more resistant to compaction. The evolution of compressive force, elastic recovery rate, particle interaction, stress tensor, and coordination number between active particles and current collector under incremental reduction were quantitatively studied in conjunction with the analysis of the morphology evolution of the deformation zone. Furthermore, the increase of the electronic conductivity is related,

however, to the conductive path inside the electrode is improved, that is, the number of contacts between particles increases, and, on the other hand, to the tightening of the contact between the coating and the current collector. The electrodes were manufactured under incremental line load. Based on the experimental data, a predictive model was supplemented using the Heckel equation for building the relationship between electrode thickness, porosity, density, and line load. The deformation mechanism during the calendering process was summarized according to the electrode morphology: particle pulverization, secondary particle fusion, PVDF network compression, and the surface deformation of the current collector. At a high line load, the surface of the current collector is embedded with active particles and deforms, increasing surface roughness.

Data availability

The data that support the findings of this study are available from the corresponding author, Huagui Huang, upon reasonable request.

CRediT authorship contribution statement

Junpeng Zhang: Methodology, Formal analysis, Software, Investigation, Writing – original draft. **Huagui Huang:** Project administration, Methodology. **Jingna Sun:** Methodology, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

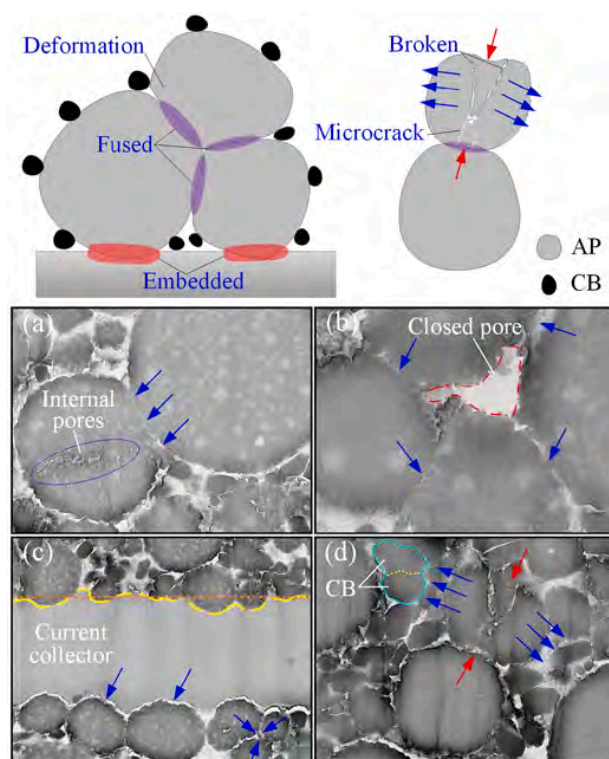


Fig. 19. Mechanism of morphological change during calendaring process. (a) The internal pores and secondary particle fusion; (b) Closed pore; (c) Surface deformation of the current collector; (d) Carbon black–PVDF compression and particle rupture.

Data availability

Data will be made available on request.

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