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Deformation and stresses in solid-state composite battery cathodes



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Mechanical behavior of solid-state cathode is simulated with a new method.
- Bending deformation of the composite cathode is highly sensitive to its thickness.
- Material selection is important to the resulting sintering and cycling stresses.
- Mechanical degradation can be mitigated by optimizing the initial composition.

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ABSTRACT

Differences in thermal contraction/expansion and volume changes during discharge/charge cycles lead to internal stresses that ultimately cause degradation of solid-state composite cathodes and hinder the realization of their practical applications. We employ the smoothed boundary method to solve the mechanical equilibrium equation for the residual stresses induced by cooling from the sintering temperature and by (de)lithiation in polycrystalline composite microstructures that are similar to realistic solid-state composite cathodes. The overall deformations of the composite slabs under these fabrication and operation conditions are also evaluated. The effects of cathode thickness and selections of different cathode materials on the resulting residual stresses and deformations are examined. We find that the (de)lithiation stresses during cycling are more than twice the thermal residual stresses after sintering. Furthermore, the maximum (de)lithiation and thermal residual stresses are sensitive to the cathode thickness only when the cathode-layer thickness is comparable to that of the electrolyte separator layer. We also investigate the impact of the lithium site fraction of the cathode particles prior to sintering on the cycling stresses and deformations, which may pave the path toward an approach to mitigating mechanically induced degradation.

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1. Introduction

Li-ion batteries are a promising platform owing to their high energy density, low self-discharge rate, and long cycle life that facilitate a wide range of applications from consumer electronics to electric vehicles [1–3]. Despite considerable progress in improving the performance of Li-ion batteries, the development of solid-state lithium ion batteries (SSBs) has become an active area of research due to their reduced risk of fire hazards compared to liquid-electrolyte-based lithium ion batteries [1,4–10]. A SSB may also enable the use of Li-metal anodes, which could boost energy density because of Li metal's high capacity. A dense solid electrolyte separator capable of suppressing the formation of Li dendrites could avoid well-known problems of internal short circuits [11]. Additionally, SSBs have the potential to achieve high power performance [8,12–14] and can offer versatile geometries [1,6,8,13,14].

Nevertheless, state-of-the-art SSBs have several limitations, including poor rate capability, capacity fade, and poor coulombic efficiency [1,2]. These limitations can be partly attributed to the low ionic conductivity of solid-state electrolytes. Therefore, the selection of solid electrolyte with high ionic conductivity is important in overcoming these issues. Li₇La₃Zr₂O₁₂ (LLZO) is a promising choice of solid electrolyte in SSBs due to its relatively high ionic conductivity compared to other candidates [15]. The ionic conductivity depends primarily on the ion conduction mechanisms and properties including valency and ionic size [16]. For example, a molecular dynamics study [17] showed that the displacive excitation events are frequent in the cubic phase of garnet LLZO and sparse in its tetragonal phase because of the difference in the conduction mechanism between the two phases. As a result, the cubic phase has an ionic conductivity in the order of 10^{-4} S cm⁻¹, which is two order of magnitude higher than that of the tetragonal phase [17]. A density functional theory study demonstrated that doping LLZO with tantalum can further enhance the lithium concentration and decrease the activation energy from 24 meV to 19 meV, which could possibly increase the ionic conductivity of the electrolyte from 10^{-3} to $10^{-2} \,\mathrm{S \, cm^{-1}}$ [18]. Additionally, LLZO's high shear modulus and chemical and electrochemical stability against Li-metal makes it suitable as a component of SSBs [15]. However, despite these advantages, the rate capability of LLZO-based SSBs with thick composite cathodes continue to fall short of expectations due to the lack of understanding of how active, conductive, and electrolyte particles function within the fabricated composite electrode. Thus, for such solid-state batteries to become a viable alternative to current battery technologies, comprehensive investigations that probe how different components and their interfaces interact within composite cathodes must be conducted. In particular, the interfaces between different components as well as the grain boundaries (interfaces between the same component) can give rise to interfacial resistance, which pose a considerable challenge that will need to be overcome.

One of the processes that contributes to the failure of oxide-based SSBs is stresses arising from fabrication and cycling. These oxidebased electrolytes can only be fused at high temperature through a process called sintering, which, for composites, can lead to significant residual stress at room temperature. Achieving mechanical stability of the electrodes in SSBs is one crucial aspect for improving their cyclability. Without such stability, the overall performance would degrade rapidly during cycling due to interfacial decohesion and other mechanical degradation. Typically, each of the components of SSB cathodes (i.e., active cathode particles, electronic conductor, and electrolyte particles) exhibits different amounts of thermal contraction on cooling after sintering that gives rise to internal stresses. For the active cathode particles, this thermal contraction is followed by additional volume changes during the charge/discharge cycles. The resulting stresses can lead to mechanical deformation, decohesion of the cathode-electrolyte interfaces, and internal fracture of active cathode particles. These mechanical instabilities in turn cause poor rate capability after cycling [1,3, 8]. Therefore, the active cathode materials in SSBs should be chosen

with additional considerations of their mechanical properties.

Lithium nickel manganese cobalt oxide (LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂, NMC) [19,20], lithium manganese oxide (LiMn₂O₄, LMO) [21], and lithium cobalt oxide (LiCoO2, LCO) [22] are among the most widely used transition metal oxide cathode materials in Li-ion batteries. Each of these materials has advantages and disadvantages, as discussed below. Lithium cobalt oxide (LCO) was the first layered transition metal oxide cathode material that achieved market success [23-25] and is still widely used in commercial batteries today [23]. However, its poor structural stability at intermediate Li composition (X < 0.5, where X is the occupancy fraction of Li sites) limits its capacity to only half the theoretical value [26,27]. Additionally, there are other disadvantages such as its high cost and negative impacts to the environment. The cubic spinel lithium manganese oxide (LMO) is an alternative with lower material cost and toxicity. However, its capacity fade due to Mn dissolution into liquid electrolyte [28] and the formation of cracks limits its practical application [29]. Layered NMC has material properties generally similar to that of LCO, but it has higher capacity because of its improved stability, leading to a wider operation range of $0.2 \le X \le 1$.

A number of theoretical investigations have been carried out to examine stress-induced degradation of SSBs [3,30-35]. For instance, Bucci et al. [30] used analytical and finite element methods to study the lithiation stress in silicon and its effects on capacity. They reported that the level of cycling stress in a solid silicon composite anode can reach 2 GPa [30], which is significantly higher than the stress of a few MPa found in a typical composite cathode with a liquid electrolyte [36,37]. In Ref. [31], the authors used a cohesive zone model to investigate the condition for damage initiation and propagation due to stress localization during Li intercalation. The effect of micro-cracking on the diffusivity of lithium and on tortuosity was investigated via a random walk analysis [32], which showed that the average Li-ion diffusivity decreases linearly with the increase in the number of micro-cracks [32]. Behrou and Maute [35] used a nonlocal damage model to simulate the damage evolution in the active cathode material using finite element method. The authors also investigated effects of the damage evolution on the mechanical and electrochemical performance of the SSBs. All the aforementioned studies attributed the poor rate capability to the fracture formation during cycling that reduces the transport properties, decreases the capacity, and weakens the mechanical integrity of the composite electrode. However, the microstructures considered in those studies are relatively simple, with composite cathodes represented as either spheres having a single size [32] or squares having a distribution of sizes [30,31] of active material embedded in a uniform solid-electrolyte matrix.

In this work, we apply the smoothed boundary method (SBM) [38] to solve the mechanical equilibrium equation to evaluate the dilatational strain and the residual stress distribution arising from thermal contraction and lattice size change due to lithiation and delithiation. This method has been successfully applied to model various phenomena in Li-ion battery cathodes, such as grain boundary diffusion [39], interparticle phase transformation [40,41], interparticle interaction [42], particle size effect [43], and surface phases of active particles [44], in lithium ion battery cathodes. The solid-state composite in our simulations represents a realistic microstructure that contains LLZO solid electrolyte, active cathode particles, and Ni as electronic conductor particles that are randomly mixed and sintered at high temperature to form a dense solid. Here, metallic Ni is chosen because of its chemical stability with transition metal oxide cathode and ceramic solid electrolyte materials at the sintering temperature and also of its mechanical properties (i.e., Young's modulus and thermal expansion rate) that are closer to those of NMC than other candidates. Three thicknesses of solid-state composite cathodes are considered (30, 60, and $120 \,\mu\text{m}$), each bonded to a 15-µm-thick electrolyte separator layer. The thermal and lithiation stresses are evaluated for the three active metal oxides (i. e., LCO, LMO, and NMC). Because of its widespread adoption in lithium ion batteries [25], NMC is further examined in our simulations for the

effect of the initial lithium composition prior to sintering on the cycling stress.

2. Model formulation

A composite cathode of a SSB consists of multiple solid materials that individually expands/contracts upon temperature changes. In addition, the active cathode particles expand/contract during lithium insertion/ extraction. To accommodate the volume changes, the composite cathode must deform, which results in internal stresses. The volume misfits can be represented by an eigenstrain, ε_{ij}^* , as introduced by Mura [45]. In this formulation, the strain is expressed as the sum of the elastic strain, e_{ij} , and eigenstrain, ε_{ij}^* [45–48]:

$$\varepsilon_{ij} = e_{ij} + \varepsilon_{ij}^*,\tag{1}$$

where, under the assumption of infinitesimal deformation, the strain is defined as a function of the gradients of displacement:

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right). \tag{2}$$

Assuming the deformation of the composite cathode due to the change in temperature or lithium concentration is in the elastic regime, the stress field, σ_{ii} , is given by the generalized Hooke's law:

$$\sigma_{ii} = C_{iikl} (\varepsilon_{kl} - \varepsilon_{kl}^*), \tag{3}$$

where C_{ijkl} is the elastic stiffness tensor. At mechanical equilibrium (*i.e.*, force balance), the stress state is governed by the mechanical equilibrium equation:

$$\frac{\partial \sigma_{ij}}{\partial x_i} = 0. \tag{4}$$

Combining Eq. (2) through (4), we obtain

$$\frac{\partial}{\partial x_j} C_{ijkl} \frac{1}{2} \left(\frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k} \right) = \frac{\partial}{\partial x_j} \left(C_{ijkl} \varepsilon_{kl}^* \right).$$
(5)

In this work, we do not specify crystallographic orientations of the grains in the polycrystalline microstructure because of the lack of experimental data for such information. We instead treat all solid phases to be elastically isotropic, which allows the fourth-order stiffness tensors in Eq. (5) to be described by the Lamé parameters. However, the general approach presented in this paper is applicable to anisotropic materials.

We apply the smoothed boundary method (SBM) to solve Eq. (5) for the displacements resulting from the mismatch between different materials due to thermal expansion/contraction as well as the volume changes of cathode materials during cycling. As derived in Ref. [38], the SBM-reformulated mechanical equilibrium equation is written as

$$\frac{\partial}{\partial x_j} \left[\psi C_{ijkl} \frac{1}{2} \left(\frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k} \right) \right] + \left| \nabla \psi \right| T_i = \frac{\partial}{\partial x_j} \left(\psi C_{ijkl} \varepsilon_{kl}^* \right), \tag{6}$$

where ψ is the domain parameter, which takes a value of one inside the solid regions and a value of zero outside the solid regions, T_i is the traction on the solid surfaces, and the subscript *i* indicates the *i*-th direction of the coordinate system. Because $|\nabla \psi|$ is only nonzero in the regions where ψ transitions from zero to one, the second term on the lefthand side exerts traction only on the solid surfaces. This term can be set to zero to impose a traction-free boundary condition, which describes a free surface.

For a solid containing multiple materials (or multiple regions of different phases), a subset of domain parameters can be used to describe the regions of different materials such that

$$\sum_{m=1}^{n} \psi_m = \psi, \tag{7}$$

where the subscript m indicates the m-th material in the solid, and n is the number of materials. The elastic stiffness tensors are different for different materials, and in such case the mechanical equilibrium equation is written as

$$\frac{\partial}{\partial x_j} \left[\sum_{m=1}^n \psi_m C^m_{ijkl} \frac{1}{2} \left(\frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k} \right) \right] + |\nabla \psi| T_i = \frac{\partial}{\partial x_j} \left(\sum_{m=1}^n \psi_m C^m_{ijkl} \varepsilon^*_{kl} \right), \tag{8}$$

where C_{ijkl}^m is the elastic constant tensor for the *m*-th material. This treatment assumes a linear interpolation of the material properties across different phases. If peak shape functions, such as $|\nabla \psi_p| |\nabla \psi_q|$ or $\psi_p \cdot \psi_q$, were included, as in Ref. [38], to modify parameters within the interfacial regions, mechanical properties of grain boundaries can also be specified. However, we here assume that the properties of a grain boundary are given by the linear interpolation between two bulk values using ψ_m because of the lack of information about grain boundary properties.

Fig. 1(a) shows the polycrystalline microstructure of the composite slab used in our simulations. This microstructure contains grains of three different size distributions associated with three materials: NMC, Ni, and LLZO. The NMC grains have a particle-diameter distribution following a truncated normal distribution with a mean of $50\Delta x$, lower bound of $45\Delta x$, and upper bound of $60\Delta x$, where Δx is the grid spacing (voxel edge size). The particle-diameter distribution of the Ni follows a truncated normal distribution with a mean at $31.5\Delta x$, lower bound at 28.5 Δx , and upper bound at 34.5 Δx . The LLZO has a particle-diameter distribution with a mean at $20\Delta x$, lower bound at $18\Delta x$, and upper bound at $22\Delta x$. The volume fractions are approximately 50%, 20%, and 30% for these three materials, respectively, in the composite cathode layer. This ratio is selected to ensure that the electrolyte phase percolates through the cathode layer to provide ionic conductivity through the composite, while the active material phase retains a large fraction to maintain a high energy capacity. The polycrystalline microstructure in the solid electrolyte layer has the same particle size distribution as LLZO in the composite cathode layer. This microstructure is described by a set of continuous domain parameters. The top portion of the slab represents a composite cathode containing grains of an active cathode material, an electronic conductor, and a solid electrolyte, as shown in the blue, green, and yellow colors, respectively. The bottom portion of the slab represents a solid electrolyte separator layer shown in yellow color. The polycrystalline microstructure was generated using an open-source software package, DREAM.3D [49]. To obtain the polycrystalline composite cathode microstructure (Fig. 1(b)), two polycrystalline microstructures (Fig. 1(c)) were first generated and then combined.

In the next step, we removed the grains whose centers of mass are above $z = 50\Delta x$ in the solid electrolyte layer, shown in the bottom panel of Fig. 1(c), to create a corrugated surface. We then replaced the voxels in the bottom region of composite cathode with those from the bottom panel. The resulting voxelated polycrystalline microstructure is shown in Fig. 1(b), which contains 1191 NMC, 1960 Ni, and 11050 LLZO particles in the composite cathode layer, and 4464 LLZO particles in the electrolyte separator layer. The interface between the composite cathode layer and electrolyte layer follows corrugated boundaries, resembling a cathode-electrolyte interface that forms during a sintering process. The vacuum region surrounding the solid slab is described by an additional domain parameter. The six faces of the slab are approximately $12\Delta x$ from the computational domain boundaries.

To reduce the number of labels required for describing the grains (sintered particles) in the polycrystalline microstructure, we employed the algorithm in Ref. [39], in which the grains not in direct contact were assigned to the same label. As a result, a total of 18665 grains required only seven, six, and ten domain parameters for NMC, Ni, and LLZO grains in the composite cathode layer, respectively, and eleven domain parameters for LLZO grains in the electrolyte separator layer. For each domain parameter, the value is set to be one at corresponding grid points



Fig. 1. (a) Polycrystalline microstructure of the composite slab described by a set of continuous domain parameters. (b) Microstructure represented by voxels for the composite cathode generated from DREAM.3D. The colors are randomly assigned to the grains to highlight the microstructure. (c) The two voxelated microstructures separately generated for (top) the composite cathode and (bottom) electrolyte separator layer. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(voxels), and zero otherwise. We then employed the polycrystalline phase field model [50] to smooth the domain parameters:

$$\frac{\partial \psi_m}{\partial t} = -L_m \Big(-\alpha \psi_m + \beta \psi_m^3 + 2\gamma \psi_m \sum_{p \neq m}^n \psi_p^2 - \kappa \nabla^2 \psi_m \Big), \tag{9}$$

where $\alpha = 1, \beta = 1, \gamma = 1.5$, and $\kappa = 0.25$. The domain parameters were smoothed for 100 steps with a time step size of 0.05. The domain parameter profiles across the solid-vacuum interface were also smoothed. Because the result from Eq. (9) does not guarantee that the sum of all domain parameters equals to one at each grid point, the resulting domain parameters were normalized with the sum of all domain parameters were normalized with the sum of all domain parameters were normalized with the sum of all domain parameters ($\psi_m = \psi_m / \sum \psi_m$). The interfacial thickness between grains was approximately three grid spacings. Here, we set Δx to be 0.3 μ m such that the slab shown in Fig. 1(a) is $180 \times 130 \times 135 \,\mu$ m³ in size, and the thicknesses of the composite cathode and electrolyte are approximately $120 \,\mu$ m and $15 \,\mu$ m, respectively.

In this work, we calculate not only the internal stresses, but also the overall deformation (*i.e.*, bending) of the composite cathode resulting from the mismatch between expansion/contraction of constituent materials during temperature and lithium concentration changes. As mentioned earlier, we introduced a vacuum region surrounding the solid such that the slab surfaces are traction free, which allows the slab to deform. Thus, we can estimate the deformation of the entire composite slab from the simulations. This treatment is different from previous micromechanics calculations, where periodic boundary conditions are imposed on the computational domain boundaries [48,51–53], which clamp the solid boundaries and prohibit global deformation of the composite cathode. This approach allows us to examine the bending of the composite cathode as described later.

3. Results and discussions

While internal stress is important in evaluating the initiation of cracks and decohesion of grains, the overall deformation of composite cathodes is also useful in optimizing the packaging of the SSBs. The internal stress states and global deformation of the composite cathode vary with the geometry of the cathode (*e.g.*, thickness) as well as different combinations of materials. Therefore, we perform simulations to examine the stress as well as deformation within composite cathodes with different thicknesses, cathode materials, and ranges of lithium concentration in the active cathode particles.

3.1. Thermal stress in composite cathodes with NMC particles

The first set of simulations examines the thermal stress in composite cathodes consisting of NMC, Ni, and LLZO due to cooling from the sintering temperature. The composite samples are assumed to be sintered at 750 °C and then cooled to 27 °C (room temperature). We assume that the interfaces between different materials are lattice incoherent in a similar treatment as thermal bending problems (*e.g.*, bending of bimetallic strips [54,55]). The thermal mismatch is calculated from the relative thermal expansion coefficient and the temperature change, as described below. Here, the strain-free state is assumed to be that of the sintered structure at the sintering temperature.

The misfit strain resulting from temperature change is given as $\varepsilon = (\alpha_1 - \alpha_2) \Delta T$ [55], where α_1 and α_2 are the thermal expansion coefficients of the two bonded materials, denoted by 1 and 2 respectively, and ΔT is the temperature change, which is 723 °C. Here, the material 2 is taken as the active cathode material. We assume an isotropic misfit strain tensor of the form $\varepsilon_{ij}^* = \varepsilon \delta_{ij}$, where the misfit strains between Ni or LLZO and NMC are $\varepsilon_{\text{Ni-NMC}} = -6.5 \times 10^{-4}$ and $\varepsilon_{\text{LLZO-NMC}} = -2.2 \times 10^{-3}$, respectively. All of the material properties employed in this work are given in Table 1.

The microstructure of the sample with a 120- μ m cathode is generated as described in the previous section, while those with 30- and 60- μ m cathodes are acquired by removing the top 3/4 and 1/2 portions of the 120- μ m cathode, respectively. The resulting microstructures are shown in Fig. 2(a)–(c).

Fig. 2(d)-(f) show the calculated fractional volume change (i.e., $\Delta V/V = \varepsilon_V \approx \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$ with the small-strain approximation) with respect to LLZO in the three composite slabs at room temperature after cooling from sintering temperature. These fractional volume changes (also called volumetric strain) indicate the constituent particles' volume contraction/expansion relative to LLZO. Thus, the LLZO particles that serve as the reference material show a blue color, indicating nearly zero relative fractional volume change. The NMC particles show colors in yellow (ε_V 5.5×10^{-3}), orange (ε_V 6.5×10^{-3}), and red (ε_V $8 \times$ 10^{-3}), which indicate a positive volume changes relative to LLZO. The positive values of ε_V , equivalent to positive misfit to LLZO, suggest that the NMC particles constrained by LLZO will be under compression in the composite slabs. Compared to LLZO, Ni has a smaller thermal contraction after cooling. Thus, the Ni particles show a positive intermediate fractional volume change relative to LLZO, as indicated by the green color ($\varepsilon_V \ 4 \times 10^{-3}$). It should be noted that we have selected Ni as the conductive agent, which has a thermal expansion coefficient and

Table 1

The materials properties used in the calculations. Note that the stiffness tensor here is in the Voight notation, where $\lambda_{11} = C_{1111}$, $\lambda_{12} = C_{1122}$, and $\lambda_{44} = C_{1212}$. The shear modulus of the materials is λ_{44} .

Constant	NMC	Ni	LLZO	LMO	LCO
Young's Modulus, E (GPa) Possion's ratio, ν $\lambda_{11} = \lambda_{12} + 2\lambda_{44}$ (GPa)	195 [19] 0.25 [19] 234	205 [66] 0.31 [66] 277	150 [19] 0.26 [19] 166	128 [21] 0.3 [21] 237	191 [22] 0.24 [22] 255
$\lambda_{12} = \frac{E\nu}{(1-\nu)(1-\Omega)} $ (GPa)	78.1	125	64.5	138	71
$\lambda_{44} = \frac{E}{2(1-2\nu)} $ (GPa)	78.1	76.3	59.5	49.6	77
$Z(1 + \nu)$ Thermal expansion coefficient α_L (K ⁻¹)	$1.25 \times 10^{-5} [19]$	$1.34 \times 10^{-5} [66]$	$1.55 imes 10^{-5}$ [67]	$1.29 imes 10^{-5}$ [60]	$1.30 \times 10^{-5} \text{[22]}$



Fig. 2. (a)–(c): The morphologies of the three solid-state composite slabs with thicknesses of (a) 45, (b) 75, and (c) 135 μ m, composed of NMC (blue), Ni (green), and LLZO (yellow). (d)–(f) The calculated fractional volume changes of the composite cathode with respect to LLZO after cooling from 750 to 27 °C. (g)–(i): The dilational stresses resulting from thermal contraction of the three solid-state composites with thicknesses of (g) 45, (h) 75, and (i) 135 μ m. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Young's modulus closer to those of the active cathode material (NMC), as compared to those of LLZO. If other conductive agents with mechanical properties more similar to those of LLZO are used, the composite cathode would mechanically behave more similarly to LLZO than the cases examined here. This would result in less bending of the slab due to less mismatch in the volume change and in more compression of the active particles.

Because of strain relaxation near the free surfaces, the color variation on the slab surfaces is greater than in the bulk. The fractional volume changes of NMC and Ni relative to LLZO on the surfaces are close to those directly calculated from eigenstrains $(3 \times 2.2 \times 10^{-3} = 6.6 \times 10^{-3})$ for NMC and $3 \times (2.2 \times 10^{-3} - 6.5 \times 10^{-4}) = 4.65 \times 10^{-3}$ for Ni). On

the contrary, mechanical constraint decreases the fractional volume changes between the three materials in the bulk, which can be clearly discerned by the much smaller color variation in the bulk of the slabs.

The residual elastic stress resulting from the cooling (also referred to as the densifying stress) is calculated using Eqs. (2) and (3). The stress state, expressed as a second-order tensor, consists of three normal and three shear stress components. While it is possible to analyze all the six stress components individually, it is more insightful to focus on relevant invariants. As a first example of such invariants, we calculate the dilatational stress (also called hydrostatic stress) using

$$\sigma_{dil} = \frac{1}{3} \left(\sigma_{xx} + \sigma_{yy} + \sigma_{zz} \right). \tag{10}$$

A negative or positive σ_{dil} indicates a compressive or tensile state, respectively. Fig. 2(g)–(i) shows the calculated σ_{dil} in the slabs. In the bulk, the LLZO shows orange (σ_{dil} ~0.12 GPa) to red (σ_{dil} ~0.23 GPa) colors, Ni shows a light blue color (σ_{dil} \sim - 0.05 GPa), and NMC shows a dark blue color (σ_{dil} \sim -0.15 GPa). These colors indicate that LLZO particles are under tension while Ni and NMC particles are under compression. On the surface, it is difficult to determine the stress state simply based on the constituent materials. Complicated microstructure effects may play some roles as shown by the results that a region with the same color can span over different types of particles on the surfaces. However, it is still observed that σ_{dil} is generally much smaller on the slab surfaces than in the bulk due to the surface relaxation; the colors on the surface mostly vary from green, yellow to light orange (σ_{dil} ranging from 0 to 0.12 GPa) with scattered areas in blue ($\sigma_{dil} \sim -0.1$ GPa), but the colors in the bulk vary from blue to red (σ_{dil} ranging from -0.15 to +0.23 GPa). In addition to the surface effect of stress relaxation, slab thickness also affects stress relaxation, which can be observed from the significantly reduced color variation in the bulk of the thin slab compared to the thick one. These observations of calculated hydrostatic stress agree with those of calculated fraction volume changes in Fig. 2 (d)–(f).

To investigate how the stress could give rise to mechanical degradation, the von Mises stress is examined, which is related to the second deviatoric-stress invariant and is calculated according to:

$$\sigma_{vM} = \sqrt{\frac{1}{2}} \left[\left(\sigma_{xx} - \sigma_{yy} \right)^2 + \left(\sigma_{yy} - \sigma_{zz} \right)^2 + \left(\sigma_{zz} - \sigma_{xx} \right)^2 + 6 \left(\sigma_{xy}^2 + \sigma_{yz}^2 + \sigma_{zx}^2 \right) \right].$$
(11)

The von Mises stress quantifies the local combined stress state of the six stress components. The results show that the areas with high von Mises stress are concentrated on the boundaries between grains of two unlike materials. This indicates that without special considerations of the mechanical properties of grain boundaries, intergranular cracks are more likely to occur than intragranular ones. The maximum von Mises stress (σ_{vM}^{M}) is found to be 0.91, 0.95, and 0.96 GPa in the 45-, 75-, and

135- μ m composite slabs, respectively, and the average von Mises stress ($\overline{\sigma}_{_{V\!M}}$) are 152, 173, and 182 MPa for these three slabs. The maximum stresses are approximately 5.5 times the average stresses due to the effect of stress concentration that stems from the abrupt variations in both material properties and grain geometries present in the composite slabs. Here, we note that the von Mises stresses are highly concentrated in some small regions, and most of the composite slabs only experience moderate stresses. The 99th percentile von Mises stresses (the maximum values after excluding the grid points having the top one percent of von Mises stress) are 0.37, 0.40, and 0.40 GPa for the 45-, 75-, and 135- μ m slabs, respectively. Hereafter, we refer to this quantity as the 99th percentile von Mises stress, denoted by σ_{VM}^{99} , and Fig. 3(a)–(c) are plotted with the color bars with these values as the maximum.

Based on a fracture size of $4 \,\mu\text{m}$ and a fracture toughness of 1 MPa \cdot m^{0.5}, the fracture stress (σ_F) of LLZO is approximated to be 300 MPa [56]. Here, we use this value as a threshold to evaluate the percentage of grid points in the samples that have von Mises stress above the fracture stress. The calculated percentages are 5.8%, 7.1%, and 7.7% for the 45-, 75-, and 135- μ m slabs, respectively. This result suggests that fewer fractures would be expected in a thinner cathode layer, but the differences are small and other features/effects may effectively mask the differences.

Fig. 4 show a series of two-dimensional sections taken at x = (a)117.0, (b) 117.3, and (c) 117.6 µm in the 75-µm slab. The grid points with von Mises stresses between σ_F and σ_{vM}^{99} are marked in a gray shade with reduced saturation to highlight those above $\sigma_{\nu M}^{99}$, which are marked in a red shade, where $\sigma_F = 300$ MPa and $\sigma_{\nu M}^{99} = 398$ MPa. We note that most of the red shaded region appears between NMC and LLZO interfaces. The grid points with stress equal to the maximum von Mises stress are indicated in the white box in Fig. 4(b), and those points are located around a multi-grain junction of NMC and LLZO grains. Our simulation results resemble some of the observations regarding the geometric effects on stress concentration in battery cathodes reported previously. For example, a finite element simulation of cathodes consisting of NMC particles indicated that largest stresses arising from volume changes are found to be at particle-particle contacts due to the constraints imposed by neighboring particles [57]. Additionally, during volume changes of LCO cathode particles, high stress is localized near small-scale surface features (i.e., sharp edges) [58]. These particle-particle contacts and small-scale surface features in those liquid cells are similar to the grain boundaries and the grain boundary junctions, respectively, in our solid-state composite cathodes.

The overall bending deformation of a composite slab after cooling is quantified by the slab's radius of curvature (*R*) as follows. At a given *z* position within the solid region, a reference line along the *x*-direction is placed along the center point of the *x*-*y* plane. The positions of the grid points on this line are (r_x^0, r_y^0, r_z^0) , and the displacements obtained by solving Eq. (6) at those points are (u_x, u_y, u_z) . Thus, the displaced



Fig. 3. Calculated von Mises stress for composites slabs with thicknesses of (a) 45, (b) 75, and (c) $135 \,\mu$ m, corresponding to the slabs in Fig. 2(a)–(c), respectively. The color limits are set to be the $\sigma_{yyt}^{0.9}$: 0.37, 0.40, and 0.40 GPa in (a), (b), and (c), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 4. A two-dimensional section of the 75- μ m-thick slab at (a) x = 117, (b) x = 117.3, and (c) $x = 117.6\mu$ m, where the regions with stress between 300 and 398 MPa are noted with a gray shade, and the regions with stress larger than 398 MPa are noted with red shade. The stresses are induced by thermal contraction as the solid-state composite cools from sintering temperature to room temperature. The location of the grid point with the maximum von Mises stress is in the white boxed region in (b). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

positions of the reference line are $\mathbf{r} = (r_x^0, r_y^0, r_z^0) + (u_x, u_y, u_z)$. The displaced reference lines on each *x*-*y* plane at different *z* positions are similarly obtained. We then average the positions of all reference lines to calculate the overall center line: $\mathbf{\tilde{r}}^x = (\bar{r}_x^x, \bar{r}_y^x, \bar{r}_z^x)$ in the *x* directions. Following the same procedure, we obtain the overall center line along the *y* direction: $\mathbf{\tilde{r}}^y = (\bar{r}_x^y, \bar{r}_y^y, \bar{r}_z^y)$. Fig. 5(a) shows $\mathbf{\tilde{r}}^x$ (solid line) and $\mathbf{\tilde{r}}^y$ (dashed line) relative to the center planes of the 45-, 75-, and 135- μ m slabs in red, blue, and green colors, respectively. These curves are similar to downward parabolas, where the bending results from the higher shrinkage of the LLZO layer than that of the composite cathode region. As expected, the thinnest slab bends the most, while the thickest one withstands the contraction of electrolyte layer most and bends the least.

The curvatures of $\tilde{\mathbf{r}}^x$ and $\tilde{\mathbf{r}}^y$ curves are calculated according to

$$K_{x} = \left| \frac{\partial^{2} \tilde{r}^{x} / \partial^{2} x}{\left(1 + \left(\partial \tilde{r}^{x} / \partial x \right)^{2} \right)^{3/2}} \right| \text{ and } K_{y} = \left| \frac{\partial^{2} \tilde{r}^{y} / \partial^{2} y}{\left(1 + \left(\partial \tilde{r}^{y} / \partial y \right)^{2} \right)^{3/2}} \right|,$$
(12)

respectively, using the finite difference method, and the corresponding results are shown in Fig. 5(b). For the 75- and 135- μ m slabs, abrupt increases of curvature are observed in the regions near the four sides of the slabs ($x, y < 30 \ \mu$ m and $x, y > 150 \ \mu$ m), indicating severe warping near the four lateral free surfaces of the slabs. The values of curvature in these regions are excluded in evaluating the overall radius of the deformed slab. Away from the free lateral surfaces ($30 < x, y < 150 \ \mu$ m), the variation of local curvature can be observed as in Fig. 5(c), which reflects the effect of microstructures. The radii of curvature of the slabs are calculated by averaging 1 / K_x and 1 / K_y , and are found to be 2.9, 6.5, and 13.8 cm for the 45-, 75-, and 135- μ m slabs, respectively, where an increase in *R* indicates a less overall deformation with increased

thickness. The bending of the slab may be important for manufacturing and packaging considerations.

The variations in overall deformations between the slabs with different thicknesses also explains the correlation between the amplitude of residual stress and sample thickness. The micromechanical stress contains a homogeneous part and an inhomogeneous part [48,59], where the homogeneous stress stems from the global deformation of the entire object and the inhomogeneous stress results from the local inhomogeneity in materials. For the thin slab, the large global deformation that takes place allows the cathode region to relieve the homogeneous stress more effectively than for the thick slabs. Thus, both the maximum and average stresses decrease in the thin slab. Here, one should note that if the samples are restricted from freely deforming as in typical micromechanical calculations, the homogeneous stress will be independent of sample thicknesses. In such cases, the calculated residual stress cannot reflect the effect of sample thickness.

3.2. Thermal stress in cathodes with different active particles

In this section, we compare the mechanical responses to cooling and subsequent delithiation of three slabs that contain NMC, LMO, and LCO as the cathode particles. All other conditions, such as sintering temperature, microstructure and boundary conditions, remain the same as in the previous section. The thickness of the composite slab is 75 μ m, a reasonable thickness for practical applications, with the composite cathode layer occupying the top 60 μ m.

As in Section 3.1, the elastic constants of LCO and LMO are assumed to be isotropic. The mechanical and thermal properties of LMO and LCO are given in Table 1. The lattice constant change of $Li_{0.92}Mn_{1.92}O_4$ measured by XRD [60] from 750 °C to 27 °C is used as an approximation to calculate the thermal mismatch eigenstrain for LMO. This choice is



Fig. 5. (a) The average displacements of the composite slabs (cathode and electrolyte) in the *z* direction, u_z , versus the *x* and *y* position. The red, blue, and green lines correspond to the three thicknesses, 45, 75, and 135 μ m, respectively. (b) The curvatures calculated using Eq. (12). (c) A magnification of curvatures from 0 to 1×10^{-4} of (b). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

made because, to the best of our knowledge, the measurements of Li_{0.92}Mn_{1.92}O₄ are the only available data in the literature over the temperature range studied in the present work. In addition, experimental observations have shown that the thermal expansion coefficient is insensitive to the Li fraction in another spinel metal oxide (Li_XMn_{1.5}.Ni_{0.5}O₄) [61] that has the same crystal structure as LMO. The thermal misfit strains for the LMO composite are $\varepsilon_{\rm Ni-LMO} = -3.6 \times 10^{-4}$ and $\varepsilon_{\rm LLZO-LMO} = -1.9 \times 10^{-3}$, calculated using the material properties in Table 1. For the LCO slab, $\varepsilon_{\rm Ni-LCO} = -2.9 \times 10^{-4}$ and $\varepsilon_{\rm LLZO-LCO} = -1.8 \times 10^{-3}$ are obtained based on the quantities in Table 1.

Fig. 6(a)–(c) show the calculated von Mises stress stemming from thermal contraction of the NMC, LMO, and LCO slabs (with $\sigma_{\nu M}^{99}$ as the maximum of color bars). The stress distributions in the three slabs are similar because the microstructure is the same. However, the magnitudes are significantly different because of the difference in material properties. For instance, the NMC sample exhibits a maximum von Mises stress ($\sigma_{\nu M}^{M}$) of 0.95 GPa, while $\sigma_{\nu M}^{M}$ in the LMO and LCO samples are 0.67 and 0.78 GPa, respectively. The $\sigma_{\nu M}^{99}$ from the simulations are 0.40, 0.33,

and 0.33 GPa for the NMC, LMO, and LCO slabs, respectively. The average von Mises stresses ($\bar{\sigma}_{\rm VM}$) over the entire LMO, LCO, and NMC slabs are 156, 150, and 173 MPa, respectively. While NMC and LCO have similar elastic properties, the magnitude of thermal misfit strain $\varepsilon_{\rm LLZO-NMC} = -2.2 \times 10^{-3}$ is larger than that of $\varepsilon_{\rm LLZO-LCO} = -1.8 \times 10^{-3}$. As a result, all three quantities associated with the von Mises stress mentioned above in the NMC slab are higher than that in the LCO. Although the magnitude of $\varepsilon_{\rm LLZO-LCO} = -1.9 \times 10^{-3}$ is larger than that of $\varepsilon_{\rm LLZO-LCO}$, the softer LMO particles (with E = 128 GPa) yields lower $\sigma_{\rm VM}^{M}$ than that in the LCO slab.

Fig. 6(d) shows the calculated displacements along the x (solid line) and y (dashed line) directions for NMC, LMO, and LCO, indicated by the blue, red, and green colors, respectively. The thermal-contraction-induced bending is similar between these three slabs, and the resulting radii of curvature are 6.4, 6.9, and 7.4 cm for NMC, LMO, and LCO, respectively. The NMC slab bends the most and LCO slab bends the least because NMC and LCO have the largest and smallest thermal misfit strains, respectively, in this calculation. The shapes of calculated



Fig. 6. The von Mises stresses resulting from thermal contraction for three different active cathode materials: (a) NMC, (b) LMO, and (c) LCO, all with a thickness of 75 μ m (60- μ m cathode on 15- μ m LLZO). The maxima of color bars are set to be the σ_{VM}^{99} of each case. (d) The averaged displacements of the composite slabs along *z* direction, u_z , versus the *x* and *y* position after thermal contraction. The blue, red, and green curves correspond to NMC, LMO, and LCO, respectively. (e) The displacements induced by Li composition change from X = 0.9 to X = 0.3, subsequent to thermal contraction. The σ_{VM} resulting from delithiation from X = 0.9 to X = 0.3 for (f) NMC, (g) LMO, and (h) LCO, with color bar maxima at the σ_{VM}^{99} of each case. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

curvatures of the LMO and LCO slabs are in general similar to that of NMC (shown in the blue curves (NMC) in Fig. 5(b)), thus, we do not present the results repetitively.

3.3. Delithiation stress with different active particles

In this section, we evaluate the stress resulting from delithiation subsequent to thermal contraction. For calculating delithiation stress, the lattice contraction/expansion of the cathode particles due to Li concentration change is included into the eigenstrain.

Upon complete delithiation ($X = 1 \rightarrow 0$, where X is the Li occupancy fraction), volume of NMC decreases by 3.4% ($\varepsilon_V = -3.4\%$) [62]. The volume contraction of LMO is 7.6% [63], which is more than double that of NMC. LCO is different from the other two materials; its volume expands by 1.6% with delithiation from X = 1 to 0.3 [64]. Here, we calculate the residual stress and deformations of the slabs after delithiation from X = 0.9 to X = 0.3 subsequent to thermal contraction, where X = 0.9 is taken as the initial Li composition of the cathode particles at sintering.

Fig. 6(g)–(h) show the calculated von Mises stresses (with σ_{VM}^{99} as the maximum of color bars), in which σ_{VM}^{99} are 0.88, 2.80, and 1.07 GPa for NMC, LMO, and LCO, respectively. The value of σ_{VM}^{M} for LMO is 6.47 GPa and $\overline{\sigma}_{VM}$ is 1.15 GPa. Compared to the LMO slab, the maximum and average stresses in the NMC and LCO slabs are significantly smaller, where σ_{VM}^{M} are 2.11 and 2.56 GPa, and $\overline{\sigma}_{VM}$ are 357 and 457 MPa, respectively. Even though LMO is the softest material among the three examined, its large volume contraction results in a much higher stresses than in the other two materials. Here, despite the fact that the von Mises stresses are all positive quantities, the LCO particles are under compression due to volume expansion, while NMC and LMO particles are under tension.

Compared to the cases with only thermal contraction, the delithiation-induced deformations are more severe in all three cases. As shown in Fig. 6(e), the NMC and LMO slabs bend upward, i.e., the opposite direction from their configurations after cooling (in Fig. 6(d)). Due to the large delithiation-induced volume contraction, the displacements of the LMO slab is almost twice that of NMC. Different from NMC and LMO, delithiation results in expansion of LCO, which leads to additional bending in the same direction as the thermal contraction alone. The radii of curvature are calculated to be -4.7, -1.1, and 2.9 cm for NMC, LMO, and LCO, respectively, where the minus signs indicate upward bending. The delithiation changes R of the NMC slab from 6.4 to -4.7 cm, LMO slab from 6.7 to -1.1 cm, and LCO slab from 7.4 to 2.9 cm. Overall, the simulation results indicate that the residual stresses and deformations induced by Li concentration changes during operations are significantly greater than those from sintering. Moreover, the results demonstrate that the material selection is of great importance. For example, delithiation of NMC and LMO offset the deformation after sintering, while that of LCO enhances the deformation after sintering.

3.4. Mitigating cycling stress of composite cathode

As demonstrated in the previous section, the effect of Li concentration change dominates the overall residual stress and deformation of the composite slabs. In principle, it is possible to find an initial Li concentration of the cathode particles that leads to the minimal stress and deformation in the operation range (*e.g.*, 0.3 < X < 0.9 for NMC). Such an approach of using a partially delithiated cathode material is uniquely suited for a SSB that uses a Li metal anode. Cells using Li metal anodes typically require a thin layer of pre-deposited lithium on the anode current collector for more facile nucleation of lithium during charging. In lithium ion cells, any deviation from full lithiation of the cathode proportionately reduces the capacity of the cell since no additional lithium is provided in the cell. Here, we calculate the overall stress and deformation of 75- μ m NMC slabs for various initial Li concentrations. Although the elastic moduli vary with Li concentration [65], we use the values for fully lithiated NMC in the calculations for simplicity. Note here we have assumed partially delithiated NMC are chemically stable during sintering for the parametric study. The thermal stability of partially delithiated NMC with the presence of LLZO during sintering requires further experimental verification. The approach, however, will be applicable to other materials that exhibit such stability.

In typical fabrication processes, composite cathodes are sintered with fully lithiated cathode particles ($X_0 = 1$, where X_0 is the Li composition at sintering). For NMC, the volume decreases by 1.76% ($\varepsilon_V = -1.76\%$) at X = 0.3 and by 0.09% ($\varepsilon_V = -0.09\%$) at X = 0.9 with respect to the fully lithiated state. The simulated von Mises stress distribution for these two cases are shown in Fig. 7(a) and (e), respectively, with σ_{VM}^{99} as the maxima of color bars. The maximum von Mises stresses after delithiation to X = 0.3 and X = 0.9 are 2.24 and 0.81 GPa, respectively. The σ_{VM}^M at X = 0.3 is approximately three times greater than that at X = 0.9. Thus, delithiation to X = 0.3 significantly increases the chance of fracture and eventual capacity fade.

If X_0 is between 0.3 and 0.9, delithiation ($X_0 \rightarrow 0.3$) and lithiation $(X_0 \rightarrow 0.9)$ lead to tension and compression, respectively, in the NMC particles. In either lithiation or delithiation, the amplitude of stress and deformation would be smaller than those stemming from monotonic delithiation (X = 0.9 to X = 0.3). Below, we analyze the cases with different X_0 , which corresponds to partially delithiated cathode particles (PDP) being used for sintering and then delithiating/lithiating to the final Li concentrations. Results for three PDP concentrations are presented here: $X_0 = 0.9$ ($\varepsilon_V = -1.64\%$ at X = 0.3), $X_0 = 0.83$ $(\varepsilon_V = -1.26\%$ at X = 0.3 and $\varepsilon_V = +0.38\%$ at X = 0.9), and $X_0 = 0.68$ ($\varepsilon_V = -0.82\%$ at X = 0.3 and $\varepsilon_V = +0.82\%$ at X = 0.9). The simulated σ_{vM} distributions are shown in Fig. 7, where (b)–(d) are for delithiation from $X_0 = 0.9$, 0.83, and 0.68 to X = 0.3, respectively, and (f)-(h) are for lithiation to X = 0.9 (except for $X_0 = 0.9$ case, which is identical to the initial state). Although the stress distributions are complicated, the patterns are quite similar because the microstructure is the same in all calculations. After delithiation, the NMC particles are under tension in (b)-(d), and $\sigma_{\nu M}$ decreases as X_0 decreases since the amplitude of ε_V decreases. Upon relithiation, the NMC particles in (g) and (h) are under compression, where $\sigma_{\nu M}$ increases as X_0 decreases. Note that the stress in (f) is purely from thermal contraction.

The results of stress calculations are summarized in Fig. 7(i)-(k), in which (i) and (j) show the average and the maximum von Mises stresses, respectively, at X = 0.3 (blue line) and X = 0.9 (black line). Note that additional data points for $X_0 = 0.84$ are included in these figures. As PDP concentration changes from 1 to 0.68, $\overline{\sigma}_{\nu M}$ and $\sigma^{M}_{\nu M}$ at X = 0.3decrease monotonically, while they monotonically increase at X = 0.9. For both $\overline{\sigma}_{vM}$ and σ^M_{vM} , the blue and black curves intersect between $X_0 =$ 0.83 and 0.84. The $\sigma_{\nu\!M}^{99}$ follow a similar pattern as in (i) and (j), and thus we do not plot them here. These results indicate that if we select PDP at a concentration near 0.83 for sintering, the amplitude of $\sigma_{\rm VM}$ induced by delithiation and lithiation will be approximately equal. This stress amplitude is significantly smaller than that of the $X_0 = 0.9$ case while retaining the same capacity, 60% of the theoretical value. Fig. 7(k) shows the percentage of grid points with σ_{vM} greater than 300 MPa (the criterion for fracture presented in Section 3.1), in which the curves follow a similar pattern as in (i) and (j). The result implies that $X_0^{\sim}0.83$ can lead to a minimum overall chance of fracture for Li concentration variation between X = 0.3 and 0.9.

Deformations of slabs made of PDP with different X_0 upon delithiation/relithiation are shown in Fig. 8, in which the solid and dashed lines are along the *x* and *y* directions, respectively. Subfigures (a) through (d) correspond to $X_0 = 1$, 0.90, 0.83, and 0.68, respectively. For the slab with $X_0 = 1$, delithiation to X = 0.3 leads to a large upward bending, as indicated by the blue curves in Fig. 8(a). Lithiation to X = 0.9 alleviates the upward bending back to a downward bending that is slightly less



Fig. 7. The effect of different initial Li compositions: $X_0 = 1$, 0.9, 0.83, and 0.68, cycling to two final Li compositions: X = 0.3 (a)–(d), and X = 0.9 (e)–(h). X_0 and X are indicated at each image from (a) to (h). The color bar maxima are set at the σ_{VM}^{99} of each case. The composite slab is of 75 μ m (60 μ m cathode on 15 μ m LLZO). The *x*-*y*-*z* labels of the plots were removed for clarity. (i) The average and (j) maximum von Mises stresses with different initial Li concentrations, X_0 , and delithiation to X = 0.3 (blue line) or lithiation to X = 0.9 (black line). (k) The percentage of grid points with stress higher than 300 MPa at X = 0.3 and X = 0.9 versus different X_0 . From the three analyses, the delithiation and lithiation stresses at X = 0.3 and X = 0.9 could be balanced if $X_0 = 0.83$ is selected. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

than that caused by thermal contraction, as shown by the green curves. The overall bending behavior of the slab with $X_0 = 0.9$, shown in Fig. 8 (b), is similar to the previous case in Fig. 8(a), but upon lithiation the slab returns to its original state after sintering. When we set $X_0 = 0.83$ for PDP, delithiation to X = 0.3 results in a significantly smaller upward bending than that in the previous two cases, while lithiation to X = 0.9 results in a larger downward bending than the original state after sintering (see Fig. 8(c)). Finally, for the case with $X_0 = 0.68$, the slab remains bent downward upon delithiation to X = 0.3 (see the red curves in Fig. 8(d)). Lithiation to X = 0.9 causes a further downward bending that is most severe among the four presented cases. Analogous to the finding from Fig. 7, it is possible to distribute the degree of bending evenly to upward and downward directions by properly selecting a value of X_0 .

The radii of curvature of slabs undergoing delithiation to X = 0.3 and lithiation to X = 0.9 are -4.3 and 7.2 cm for $X_0 = 1$, -4.7 and 6.4 cm for $X_0 = 0.9$, -7.0 and 4.4 cm for $X_0 = 0.83$, and 12.7 and 3.3 cm for $X_0 = 0.68$, respectively. The minus signs indicate upward bending. To demonstrate the resulting shapes of the slabs, we plot arcs corresponding to these radii in Fig. 8(e) through (h), in which the arc lengths are 2.54 cm. These results demonstrate that degrees of upward and downward bendings can be controlled during cycling by optimizing a value of

 X_0 . Furthermore, it is also possible to design a slab that is flat at the delithiated state; for example, the slab $X_0 = 0.68$ is nearly flat at X = 0.3.

4. Conclusion

In this paper, we evaluated the stress state and deformation of solidstate composite cathodes due to thermal contraction and cycling. The simulations were performed by solving the mechanical equilibrium equation with realistic microstructures in a model system consisting of a dense, solid LLZO electrolyte separator layer bonded to a dense composite cathode consisting of LLZO, Ni, and cathode particles. Composite cathodes of three thicknesses (30, 60, and $120 \,\mu$ m) with a 15- μ m-thick separator layer, as well as three different active cathode materials (NMC, LMO, and LCO), were examined. The results showed that the maximum residual von Mises stress induced by sintering and subsequent cooling is moderately insensitive to the thickness, ranging from 0.91 GPa for the 30- μ m-thick composite to 0.96 GPa for the 120- μ m-thick composite. However, the overall shape change, as quantified by radius of curvature, was found to be highly sensitive to thickness and was several times larger for the 30- μ m-thick composite than that of the 120- μ m-thick



Fig. 8. The displacements, u_z , at different *x* (solid line) and *y* (dashed line) positions of the slabs with different PDP values: $X_0 = (a) 1$, (b) 0.9, (c) 0.83, and (d) 0.68. The slabs are delithiated and relithiated to the end Li concentrations at X = 0.3 (blue) and X = 0.9 (green), respectively. The displacements resulting from thermal contraction are plotted in red. (e)–(h) Arcs corresponding to the radii of curvature from the simulations present in (a)–(d), respectively, are plotted with lengths of 2.54 cm. The colors correspond to the legends in (a)–(d). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

composite. The bending of the slab may be important for manufacturing and packaging considerations where stacking of flat curved slabs could lead to fractures. The thermal stress in the cooled slab with a NMC cathode was larger than LMO and LCO. However, we found that the LMO cathode suffers from much higher delithiation-induced stress compared to the other two active materials. NMC exhibited the smallest delithiation stress among the three materials, and thus we further examined the delithiation/lithiation-induced stresses in NMC slabs. Our results demonstrated that delithiation and lithiation stresses could be reduced by selecting an intermediate initial Li concentration for the NMC particles prior to sintering. We found the approximate optimal value to be $X_0 = 0.83$. The results suggested that mechanical degradation and subsequent loss of electrochemical performance could be partially mitigated by the optimization of the initial composition of the active cathode material. This approach could be uniquely suited to SSBs incorporating Li metal anodes, where the loss of lithium in the cathode could be offset by providing a thin initial layer of Li metal that can also serve to improve nucleation of Li during charge.

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