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Oxygen Release Induced Chemomechanical Breakdown of Layered Cathode Materials

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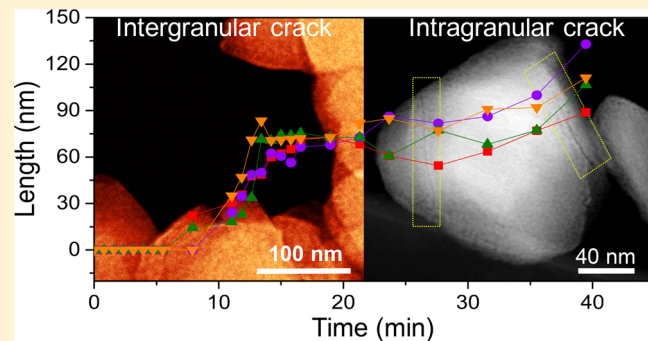
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Supporting Information

ABSTRACT: Chemical and mechanical properties interplay on the nanometric scale and collectively govern the functionalities of battery materials. Understanding the relationship between the two can inform the design of battery materials with optimal chemomechanical properties for long-life lithium batteries. Herein, we report a mechanism of nanoscale mechanical breakdown in layered oxide cathode materials, originating from oxygen release at high states of charge under thermal abuse conditions. We observe that the mechanical breakdown of charged $\text{Li}_{1-x}\text{Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ materials proceeds via a two-step pathway involving intergranular and intragranular crack formation. Owing to the oxygen release, sporadic phase transformations from the layered structure to the spinel and/or rocksalt structures introduce local stress, which initiates microcracks along grain boundaries and ultimately leads to the detachment of primary particles, *i.e.*, intergranular crack formation. Furthermore, intragranular cracks (pores and exfoliations) form, likely due to the accumulation of oxygen vacancies and continuous phase transformations at the surfaces of primary particles. Finally, finite element modeling confirms our experimental observation that the crack formation is attributable to the formation of oxygen vacancies, oxygen release, and phase transformations. This study is designed to directly observe the chemomechanical behavior of layered oxide cathode materials and provides a chemical basis for strengthening primary and secondary particles by stabilizing the oxygen anions in the lattice.

KEYWORDS: Cathode, crack, phase transformation, oxygen release



Since the inauguration of implementing LiCoO_2 materials in commercial lithium ion batteries, a number of cathode materials derived from LiCoO_2 have been investigated and applied in practical batteries. In particular, $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC) materials, with Ni and Mn cosubstituting the Co site in LiCoO_2 , are regarded as the most promising LiCoO_2 derivatives that can potentially improve practical energy density, reduce cost, and enhance safety characteristics of batteries for fast-growing applications, such as electric vehicles and grid energy storage.¹⁻³ However, challenges at the length scales of active particles,^{4,5} electrodes,⁶⁻⁹ and interfaces in full cells¹⁰⁻¹² have decelerated the pace of their substitution for the

expensive LiCoO_2 in the market. Stoichiometric NMC 49 materials usually consist of nanometric primary particles 50 assembled into 3D hierarchical structures (larger secondary 51 particles).¹³⁻¹⁶ Performance degradation of cathodes contain- 52 ing NMC materials may be attributed to formation of 53 microcracks between primary particles,¹⁷ electrolyte decom- 54 position,^{18,19} undesired phase transformations such as surface 55 reconstruction,^{4,5} and dissolution of transition metal cations.²⁰ 56

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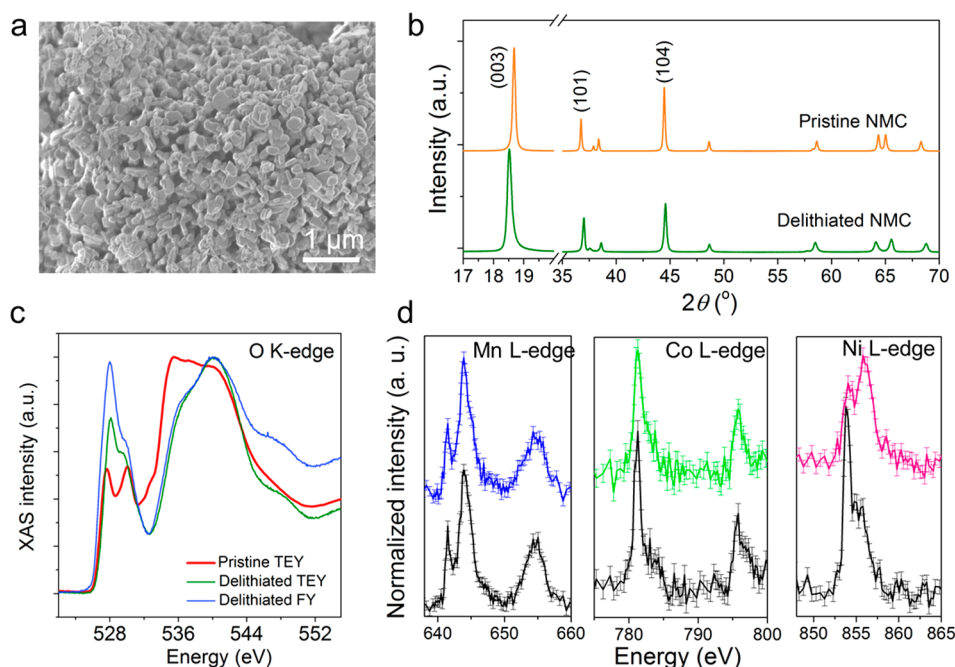


Figure 1. (a) SEM image of the pristine NMC material. (b) XRD patterns of pristine and delithiated NMC materials. (c) O K-edge XAS collected in the TEY and FY modes for pristine (red/TEY) and delithiated (green/TEY and blue/FY) NMC materials. (d) TM L-edge XRS of pristine (bottom) and delithiated (top) NMC materials. The error bars were calculated based on the standard deviations of six repeated data acquisitions under identical experimental conditions.

57 These processes are highly correlated at the atomic scale.
 58 Because of the hybridization between transition metal (TM) 3d
 59 and O 2p orbitals and local coordination chemistry in oxide
 60 cathode materials (including NMCs), d holes generated during
 61 lithium deintercalation partially reside on O 2p orbitals, which
 62 activates oxygen anions,^{21–23} accelerates electrolyte oxidation,
 63 and results in reduced transition metal oxides on particle
 64 surfaces, e.g., rocksalt formation.^{4,24,25} The volume change upon
 65 charging/discharging causes local stresses that can induce
 66 microcracks in 3D hierarchical NMC structures.^{26,27} Micro-
 67 cracks increase the exposed surface area to electrolytic solution
 68 leading to more severe electrolyte oxidation and rocksalt
 69 formation, especially at high operating voltages.²⁸ The
 70 aforementioned challenges prevail in almost all oxide-based
 71 cathode materials.^{4,25,26,28,29}

72 Crack formation has been reported in many studies as one of
 73 the important failure mechanisms in battery cathodes.^{27,30–32}
 74 Their formation is generally categorized as either intragranular
 75 or intergranular, where the former occurs within the primary
 76 particles, and the latter occurs along grain boundaries, i.e., in
 77 between primary particles. Yan et al. reported intragranular
 78 crack formation in a commercial $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ material
 79 when charged up to 4.7 V in lithium half cells, which are closely
 80 related to dislocations.²⁶ Intragranular cracks were also
 81 observed in Li-rich and Mn-rich cathode materials, resulting
 82 in voltage decay and capacity fade.^{29,33} Crack formation can be
 83 attributed to the periodic lattice expansion and contraction
 84 upon long-term cycling, similar to the fatigue phenomenon in
 85 materials under cyclic loading. Oxygen activity and gas release
 86 phenomena are frequently observed in lithium-rich layered
 87 oxide cathode materials.^{21,23} For stoichiometric NMC materi-
 88 als, however, it is somewhat unclear and debatable how much
 89 oxygen activity functions in the charge compensation.^{34,35}
 90 Nevertheless, it is the general consensus that depleting O 2p
 91 orbitals can result in the oxidation of electrolyte and reduction

of transition metals at the surface of NMC particles.^{4,24,36} 92
 Furthermore, depleting O 2p orbitals increases the risk of 93
 oxygen gas release under thermal abuse conditions, especially at 94
 high states of charge.³⁷ Apart from safety concerns,³¹ the phase 95
 transformation that arises from oxygen release creates local 96
 stresses that can potentially lead to the chemomechanical 97
 breakdown, namely, formation of microcracks.³⁸ 98

Herein, by virtue of *in situ* environmental transmission 99
 electron microscopy (ETEM), we studied the morphology 100
 transformation of charged NMC particle ensembles under 101
 thermal abuse conditions. Two distinct processes took place at 102
 the nanometric scale. First, the particle ensembles underwent 103
 intergranular crack formation at the boundaries after a short 104
 incubation period. Second, the nanopores propagated in 105
 primary NMC particles, grew to larger pores/exfoliations 106
 (intragranular cracks), and eventually led to the mechanical 107
 breakdown of primary particles. Throughout the entire process, 108
 we observed continuous reduction of transition metals, 109
 formation of spinel/rocksalt phases, as well as oxygen release. 110
 The oxygen release accelerates the mechanical breakdown of 111
 delithiated NMC materials. Meanwhile, finite element model- 112
 ing was performed to provide insights into the formation and 113
 propagation of the oxygen release and subsequent chemo- 114
 mechanical breakdown of NMC cathode materials. Finally, 115
 complementary to the *in situ* heating with TEM visualization, 116
 we observed extensive crack formation in secondary particles 117
 using transmission X-ray tomography for particles after long- 118
 term cycles. Our study highlights the importance of controlling 119
 local stresses in 3D NMC hierarchical structures at high states 120
 of charge under thermal abuse conditions. 121

Characterization. Battery materials inevitably operate 122
 outside the electrochemical stability window of the electrolytic 123
 solution, which is defined by the highest occupied molecular 124
 orbital (HOMO) and the lowest unoccupied molecular orbital 125
 (LUMO) of its constituents. Electrode–electrolyte interactions 126

127 complicate the surface chemistry of cathode materials, which
128 inevitably undermines the determination of intrinsic electro-
129 chemical properties. Chemical delithiation, in contrast, provides
130 an efficient path toward preparing charged materials without
131 the interference of electrode–electrolyte side reactions. In this
132 study, we first synthesized $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ (NMC) powder
133 using a coprecipitation method (see the [Experimental Section](#)).
134 The primary particles (100–300 nm) are agglomerated into a
135 porous architecture ([Figure 1a](#)) that allows for the rapid
136 percolation of oxidative solution during the subsequent
137 chemical delithiation. The synthesis results in NMC particles
138 with a broad distribution of morphologies. Importantly, we
139 could identify secondary particles that consisted of only a few
140 primary particles rather than big agglomerations under TEM
141 (shown later). These secondary particles are good candidates
142 for *in situ* TEM study given the limited penetration depth of
143 electron beams. The previously described chemical delithiation
144 method^{39,40} resulted in a lithium-poor NMC powder
145 (delithiated NMC), which retained the $\alpha\text{-NaFeO}_2$ layered
146 structure with the space group of $R\bar{3}m$. The (003) peak of
147 delithiated NMC shifted to a lower angle, indicating that the
148 stronger layer–layer repulsion results in expansion of the *c*-axis
149 space ([Figure 1b](#)). Due to the strong oxidation reaction, we
150 occasionally found exfoliation in the primary particles ([Figure](#)
151 [S1](#)).⁴¹ We then characterized the electronic structures of the
152 transition metal (TM) cations before and after chemical
153 delithiation via soft X-ray absorption spectroscopy (XAS) and
154 X-ray Raman spectroscopy (XRS). The TM 3d–O 2p
155 hybridization in the TMO_6 octahedral cluster gives rise to
156 distinctive pre-edge peaks between 525 and 533 eV in the O K-
157 edge XAS spectra ([Figure 1c](#)). The nature of the hybridization,
158 such as delocalization of hole states, is rather complicated and
159 under debate.⁴² Nevertheless, it is generally accepted that the
160 intensity of the pre-edge peak is in a positive relationship with
161 the total hole concentration in the TMO_6 cluster.^{34,43,44} The
162 intensity of the pre-edge peak increases after chemical
163 delithiation ([Figure 1c](#)), and exhibits a depth-dependent
164 behavior;^{26,43,45} namely, the bulk (probed by fluorescence
165 yield, FY, 50–100 nm) shows a higher hole concentration than
166 the surface (probed by total electron yield, TEY, 5–10 nm).
167 This observation is consistent with recent studies showing that
168 oxygen activity, *i.e.*, O 2p occupancy, shows depth-dependent
169 behaviors.^{24,35,43,45} X-ray Raman spectroscopy (XRS) is a
170 powerful technique to measure TM L-edge spectra with bulk
171 sensitivity. Overall, Ni experienced a dramatic increase of
172 valence state, while Mn and Co remained unchanged after
173 chemical delithiation ([Figure 1d](#)).^{34,44} It should be noted that
174 Co redox in NMC materials is still debatable. We did not
175 observe Co also likely due to the limited energy resolution of
176 XRS. Nevertheless, our study demonstrates that we have
177 successfully chemically delithiated NMC and that the charge
178 compensation is via depletion of electrons in O 2p and Ni 3d
179 orbitals (oxygen is activated). Based on the reported Ni L-edge
180 and O K-edge XAS and XRS at the given states of charge, we
181 estimated that the chemically delithiated NMC powder had
182 approximately 60% of the lithium removed.²⁴ The chemical
183 composition was then measured by the inductively couple
184 plasma–optical emission spectrometry (ICP–OES) to be
185 $\text{Li}_{0.5}\text{Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$. The chemically delithiated sample was
186 equivalent to the NMC material electrochemically charged to
187 4.3 V.^{4,46} Hereafter, we refer to the sample as delithiated NMC.
188 We chose chemically delithiated samples over the electro-
189 chemically delithiated counterparts because the former could

provide less reduced surfaces thus more oxygen release upon *in*
situ heating to amplify the observation. Such a choice does not
undermine our conclusion in this work because both samples
would release oxygen upon heating.

According to our recent study,⁴¹ chemical delithiation can
represent electrochemical delithiation in terms of the bulk
electronic structures (oxygen activation, oxidation of transition
metals). There was disintegration of secondary particles after
chemical delithiation. To observe the crack formation under *in*
situ TEM heating condition, disintegrated secondary particles
(with a few particles connected with each other) are good
because otherwise it is hard for the electron beam to penetrate
thick secondary particles. We then performed *in situ* heating
experiments on the delithiated NMC particles, using an ETEM,
to directly visualize the chemomechanical breakdown. Under
normal battery cycling conditions, the oxygen loss occurred
through the interfacial reaction between the lattice oxygen and
the electrolyte after NMC particles are electrochemically
delithiated. In this present study, we chose to perform *in situ*
TEM at 230 °C to exponentially accelerate the oxygen release
and phase transformation so that we could observe chemo-
mechanical breakdown of NMC particles within a reasonable
time frame for the *in situ* TEM observation. Z-contrast scanning
transmission electron microscopy (STEM) movies were
continuously recorded during the entire heating process (a
representative accelerated STEM movie is provided in the
Supporting Information, [Movie S1](#)). Our previous study
showed that the chemical delithiation process could introduce
microcracks ([Figure S1](#));⁴¹ thus in this study we specifically
identified particle ensembles that had no microcracks prior to
in situ heating in TEM. We tracked the nucleation and
propagation of microcracks along grain boundaries during
this early stage of chemomechanical breakdown ([Movie S1](#)).
[Figure 2a–d](#) shows four representative STEM images that
reveal the characteristic evolution of microcracks. Upon heating
at 230 °C, several slender microcracks were generated in
sporadic spots and grew quickly in length and breadth after a
short incubation period (~7 min), reaching ~70 nm at 15 min.
Then, the speed of propagation decelerated and stayed mostly
unchanged for another 15 min. Finally, the length reached
about 90 nm after 40 min. During this stage, the chemo-
mechanical breakdown took place along grain boundaries
(intergranular regions), likely due to the plethora of defects and
lattice mismatch near grain boundaries. Grain boundaries are 2-
dimensional (2D) defects, usually the weakest regions in
cathode secondary particles, and are reported to disintegrate
after long-term battery cycling.^{17,26} Notably, the above
quantification method, based on 2D STEM images, does not
fully account for the propagation of microcracks in the bulk
region of the particles, which were further investigated by three-
dimensional (3D) STEM tomography (discussed later in the
work). Our subsequent spectroscopic and finite element
analyses in this work showed that the oxygen release induced
phase transformation is the main driving force responsible for
the crack formation (see next).

In addition to the formation of intergranular cracks, pores
and layer exfoliation (intragranular cracks) were generated in
individual primary particles upon extended heating (10 h).
[Figure S4](#) shows the TEM images of these individual particles.
The relatively dark and light colors are related to the thick and
thin regions of particles (mass–thickness contrast, [Figure S4a](#)).
To enhance the visualization, we colored the thick regions with
blue and thin regions with yellow, where many nanopores of

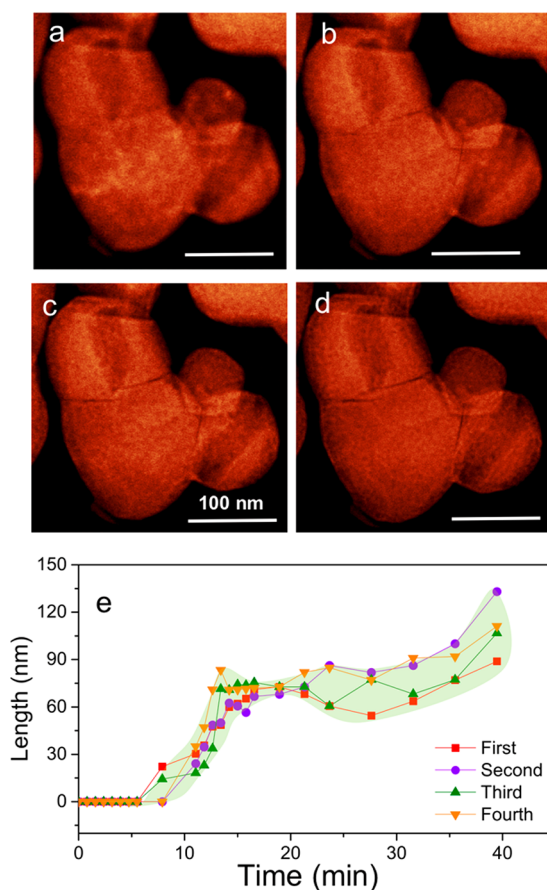


Figure 2. Selected Z-contrast scanning transmission electron microscopy (STEM) images to represent the evolution of a typical intergranular crack upon thermal activation: (a) 0, (b) 12, (c) 26, and (d) 40 min. (e) Evolution of crack length as a function of time, where four cracks (indicated by arrows in Figure S2) were independently measured and are presented here.

approximately 10 nm can be directly visualized (Figure S4b). Some of the pores link together to form a pore-cluster catkin-like morphology around the individual particles. Additionally, some particles show exfoliations (one kind of intragranular crack) (Figure S4c). Pores (surfaces) and exfoliations (most likely between (003) plane) occur inside the individual particles where the interaction between atomic layers is weak, which is a possible pathway for intragranular cracks.²⁶ Furthermore, the wrinkles pointed by arrows in Figure S4d are most likely associated with the one-dimensional local strain. Previous studies uncovered that oxygen release could lead to phase transformations of cathode particles.^{45,46} Fast Fourier transform (FFT) and inverse fast Fourier transform (IFFT) were performed to illustrate the details of phase transformation after *in situ* heating (Figure S4e,f). Regions with layered structures are isolated from the continuous spinel/rocksalt matrix (Figure S4f). The phase boundaries are random and closely accompanied by the propagation of transition metal redox transformations.⁴⁷

Electron energy loss spectroscopy (EELS) was performed on delithiated NMC and *in situ* heated NMC to further understand the underlying processes of forming microcracks. Several recent studies showed that electrochemically delithiated cathode particles displayed a gradient in the distribution of TM valence states due to the electrode–electrolyte side reactions and

surface reconstruction.^{4,47,48} Similar to the gradient distribution of hole states on the oxygen site (Figure 1c), we also observed the gradient distribution of Ni oxidation states in the delithiated particles (lower oxidation state in the surface), as shown in Figure S3. Furthermore, consistent with the O K-edge soft XAS results (Figure 1c), the O K-edge EELS underwent a red-shift in the pre-edge (TM 3d–O 2p) (Figure 3b), and the intensity of the pre-edge peak gradually increased in the first 5 nm and then leveled off (Figure 3b,c). The spatially resolved TM L-edge EELS spectra, particularly the Mn L-edge, marginally shifted to higher energy from the top surface to the subsurface, which indicates that the chemical delithiation has a similar effect on the gradient distribution of TM valence state. Since there was no electrolyte exposure in these chemically delithiated particles, we conjecture that the surface TM reduction was attributable to oxygen release when handling the sample in the glovebox. For the delithiated NMC particle after heating, EELS of three selected square (10 nm by 10 nm) regions with and without pores were collected for a comparison. We observed that the energy for the TM L-edges at the subsurface (*i.e.*, 20 nm in for pores present in the green and red rectangles) is lower than that of bulk (pore-free area in the blue rectangle) (Figure 3d,e). Therefore, the reduced layer (10–50 nm) on the heated particle is much thicker than that on the pristine (5 nm), delithiated particle, suggesting that the heating further reduces the transition metal and propagates the spinel/rocksalt layer. The pre-edge peak of the O K-edge EELS was expected to decrease due to the hybridization between TM 3d and O 2p orbitals and local coordination chemistry in oxide cathode materials.^{24,25,29,49,50}

In addition, we weighed the mass of delithiated NMC powder before and after heat treatment in the tube furnace at 230 °C for 3 h. The primary mass of the delithiated NMC powder decreased by approximately $3 \pm 1.5\%$ (mass ratio) due to the oxygen loss during the heat treatment, assuming that other elements are not volatile at such a low temperature. The oxygen release is not reversible in the present study; thus we did not observe the healing of cracks that was reported for lithium-/manganese-rich cathode materials upon electrochemical cycling.⁵¹ In practical applications, oxygen release and thermal runaway can lead to severe phase transformation of active materials, chemical decomposition of the electrolyte, and severe unmanageable safety hazards.

Intragranular cracks were also observed in individual particles after *in situ* heating by using 3D STEM tomography. Figure 4 shows four representative photographs of various viewing directions of the two primary particles. Viewing the particle at different cross sections through the 3D STEM tomography showed that a large number of pores were present at the outer surface of the particles (Figure 4 and Movie S2). However, there are two cracks of around 80 nm that are only noticeable when observing the inside of the particle from specific orientations or cross sections, which indicates that the cracks terminate in the particle (Movie S2 and Figure 4b–d). Furthermore, the small particle (Figure 4d) exfoliated due to the short element migration distance compared to the adjacent large particle, which is the direct consequence of oxygen release and structural collapse. Intragranular cracks are mainly formed due to the development, transformation, and propagation of defects, vacancies, and dislocations. More extensive and irreversible crack formation is observed by transmission synchrotron X-ray tomography for commercial NMC materials after a long period of electrochemical cycling (Figure S5). The

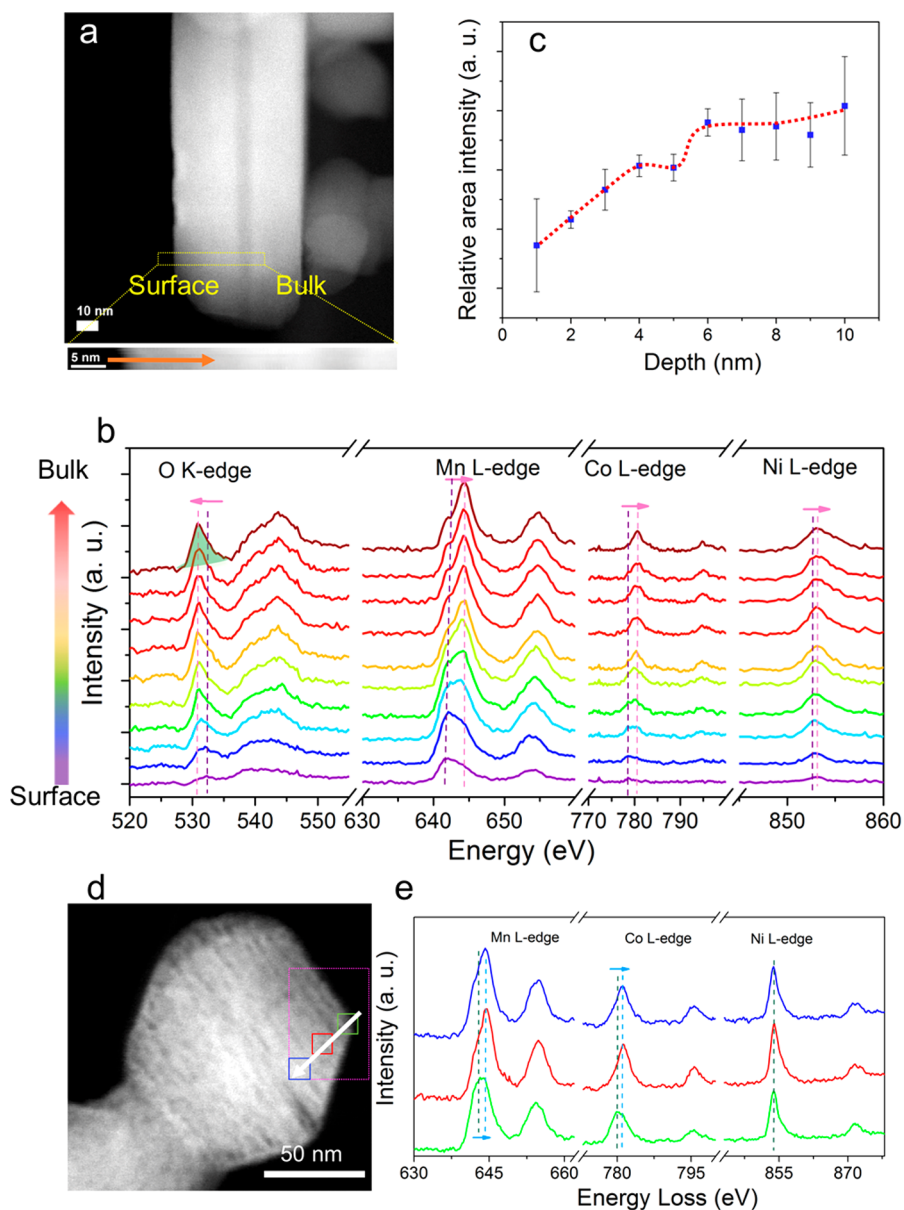


Figure 3. STEM-EELS analysis of NMC particles before (a–c) and after (d–e) thermal treatment. (a) STEM image shows the selected region on a delithiated NMC particle, where EELS spectra were collected. (b) EELS spectra of O K-edge, Mn L-edge, Co L-edge, and Ni L-edge corresponding to the selected region in part a. The line scanning direction from surface to bulk had a step size of 1 nm. (c) Normalized integrated intensity of the TM 3d–O 2p hybridization states, with the integrated intensity in a positive relationship with the hole concentration in the TMO_6 octahedral cluster. The error bars were created based on standard deviations of spectra collected at equivalent depths in three different regions of the same particle. The dashed line is added to guide the visualization. (d) STEM image shows the selected region on a thermally treated NMC particle, where EELS spectra were collected. (e) EELS spectra of Mn L-edge, Co L-edge, and Ni L-edge corresponding to the selected region in part d with identical color schemes. The energy shift of the L_3 -edge is indicated by dashed lines and arrows. The EELS spectra were calibrated based on the energy of Mn^{2+} L-edge.

341 chemical delithiation can induce crack formation due to the fact
 342 that the concentrated oxidant used to rapidly oxidize the host
 343 structure can result in stress buildup and cracks. This process
 344 occurs too rapidly to be studied by *in situ* ETEM. The crack
 345 formation during prolonged electrochemical delithiation/
 346 lithiation has been well reported by the literature, but the
 347 cracks usually accumulate after a large number of cycles (Figure
 348 SS) thus inhibiting the *in situ* ETEM study. To facilitate the *in*
 349 *situ* observation, we took advantage of oxygen release of
 350 charged NMC particles under thermally activated conditions to
 351 mimic the oxygen release and crack formation under prolonged
 352 battery cycling. For this study, we carefully chose clusters of

primary particles that were free of cracks caused by the 353
 chemical delithiation. Combining with our and other 354
 researchers' earlier finding that extensive oxygen loss and 355
 metal reduction occurred at the surface of NMC particles after 356
 long-term cycling at room temperature,^{4,31,36,52} the X-ray 357
 tomography results are consistent with the *in situ* heating 358
 observation, which validates the applicability of our finding to 359
 conventional cycling conditions. 360

Considering that the continuous electron beam radiation 361
 could potentially damage the structure^{53,54} and affect the 362
 intergranular crack and pore formation, *ex situ* heating 363
 experiments were conducted. The delithiated NMC powders 364

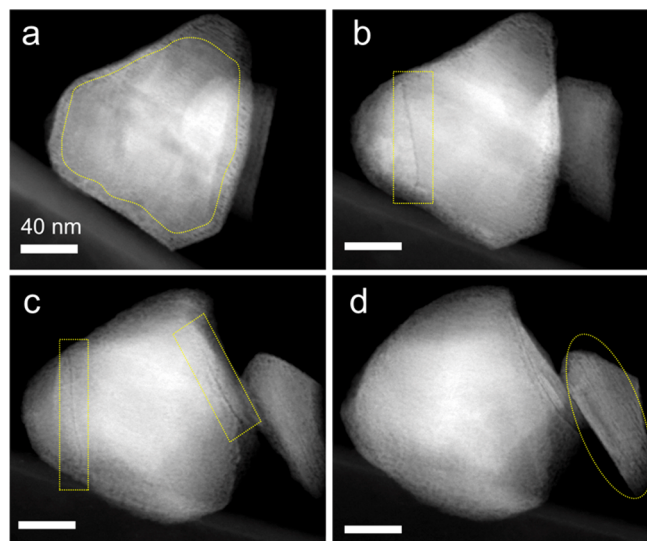


Figure 4. (a–d) STEM images for the same two particles taken from different directions to exhibit the 3D view of delithiated NMC particles after *in situ* heating on a TEM grid. The regions enclosed by yellow dashed curves display intragranular cracks. The scale bars are 40 nm for all images.

were placed in an environmental chamber and kept at 230 °C for 3 h. EELS and TEM images of the *ex situ* sample were taken to compare with the *in situ* heating sample. Note that the intergranular cracks, surface pores, and layer exfoliation were all present in the same image (Figure S6). Meanwhile, there were no major differences between the TM L-edge EELS spectra of the *in situ* heated sample and the *ex situ* heated powder (Figure S7), which means that the valence change, structural transformation, and formation of cracks are attributable to the abusive thermal conditions and not to the long-term electron beam irradiation. The present study indicates that if methods (e.g., doping, coating) can be developed to sufficiently inhibit oxygen loss upon electrochemical cycling, the chemomechanical properties of NMC materials will be improved, particularly for nickel-rich NMC materials.

The chemomechanical failure of NMC particles was theoretically studied using finite element method. The surface stress is about two orders magnitudes smaller than the bulk stress. Therefore, in the finite element modeling, we have ignored the effect of surface tension. Previous studies reported that the layered-to-spinel phase transition was accompanied by an anisotropic volumetric strain (the ratio of the lattice constants $c_{\text{hex}}/a_{\text{hex}} = 5.07$ in the layered structure decreased to 4.89 in the spinel and rocksalt phases).⁵⁵ Consequently, NMC particles aggregated with different grain orientations (Figure

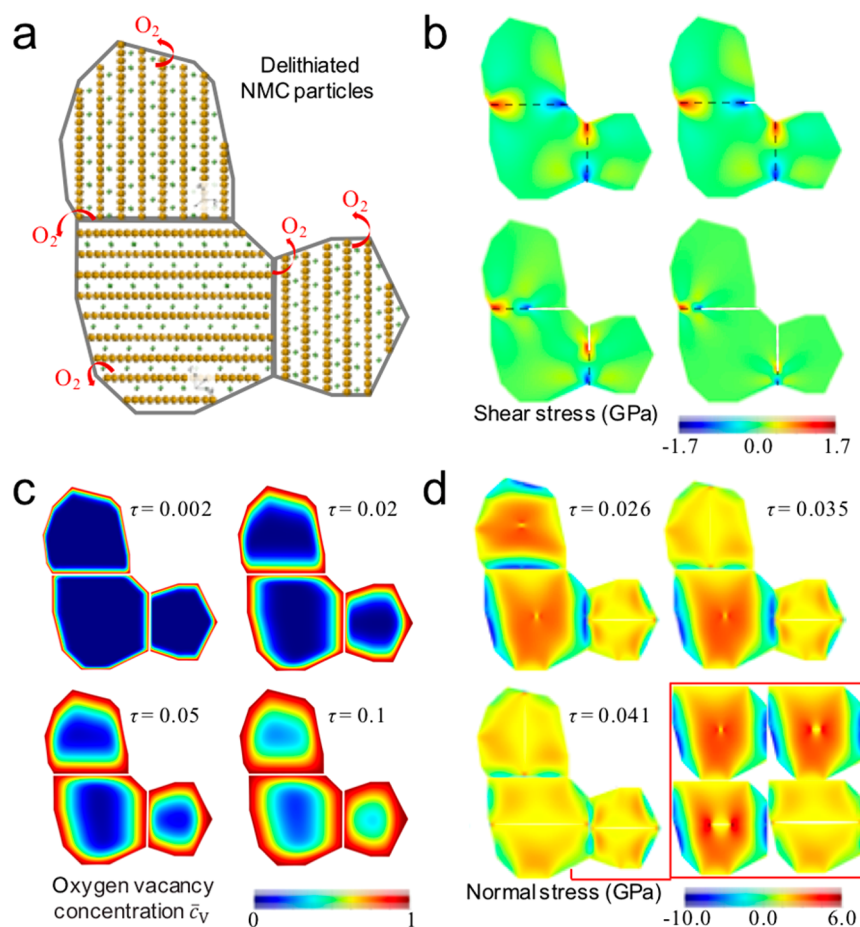


Figure 5. (a) Finite element modeling (FEM) model consisting of multiple NMC grains of different orientations. (b) Evolution of shear stress along the grain boundaries and associated intergranular cracks induced by the phase transformation of NMC. (c) Profile of the oxygen vacancies, and (d) nucleation and propagation of intragranular cracks induced by oxygen release in NMC. The inset in part d shows the initiation and rapid propagation of the intragranular crack in the lower left NMC grain.

5a) are subject to mismatch strains at the grain boundaries and shear stresses. The stress field facilitates intergranular cracks to initiate at the grain edges and rapidly propagate along the grain boundaries. Figure 5b shows the snapshots of the intergranular cracks. The shear stress is partially released after the channel cracks propagate through the grain boundaries.

Figure 5c depicts the distribution of oxygen vacancy concentration within the NMC grains as a function of the normalized time $\tau = D_{O}t/L^2$, where L represents the characteristic size of the NMC grain. The characteristic time scale for oxygen transport is much longer than that of phase transition. In addition, the chemical stability of the layered structure before the phase transition prohibits the oxygen release,⁵⁵ while the fresh surface created by the phase transition induced cracks largely accelerates oxygen release. We believe that oxygen loss mostly accompanies the phase transition. Here we model the strains and cracks induced by the phase transition and oxygen release separately. The oxygen vacancies within NMC grains are inhomogeneously distributed because of the orientation-dependent oxygen release rate.⁵⁶ Figure 5c shows the evolution of the oxygen vacancies over time. The formation of oxygen vacancies triggers considerable lattice expansion in NMC.⁵⁷ The gradient of oxygen vacancy induces a field of mismatch strain and thus stresses along the NMC grains as well as within the grains, appending the shear stresses along the grain boundaries caused by the phase transition. The resulting stress field promotes intergranular cracks. Upon oxygen release, the outer shell, which is enriched in oxygen vacancies, undergoes a larger expansion than the core regime, generating a compressive stress field near the surface and tensile stresses at the center (Figure 5d). As a consequence, the tensile stresses at the center of a grain initiate and propagate an unstable radial crack and cause breakdown of NMC grains, which are shown in the inset of Figure 5d. The nucleation and propagation direction of intragranular cracks depend on the profile of the oxygen vacancies, the geometry of NMC grains, as well as the size and orientation of the pre-existing defects. Therefore, one can safely conclude that the FEM analysis is consistent with our experimental observation, and the integrative approach of experiments and modeling offer a good path toward understanding the chemomechanical properties of cathode materials.

In conclusion, thermal and chemomechanical stability are important for evaluating lithium ion batteries in terms of their cycle life and safety characteristics. The oxygen activity and evolution in NMC cathode materials, especially when charged to high voltages and under thermal abuse conditions, can create chemical and structural transformations that directly impact the chemomechanical stability. By virtue of *in situ* ETEM and synchrotron X-ray spectroscopy, we studied the oxygen release induced chemomechanical breakdown of charged NMC materials. Specifically, we observed the formation of inter- and intragranular cracks, pores, and layer-layer exfoliation during the events of oxygen release, transition metal reduction, and structural transformation. Additionally, the growth process of intergranular cracks was quantified and monitored through the finite element modeling, which indicated that the oxygen release triggered the chemomechanical breakdown of delithiated NMC materials. The crack incubation probed by *in situ* ETEM and modeled by FEM analysis suggests that the oxygen release induced phase transformation needs to be accumulated to a certain degree before a crack can be initiated. This could potentially explain the less severe crack formation when NMC materials are cycled at lower voltages.²⁶ Although practical

batteries are operated at lower temperatures than the *in situ* heating study, our results reveal the interrelationship between orbital occupancy, and thermal and chemomechanical stability, and provide a chemical basis for future studies of the oxygen activity and safety characteristics in oxide cathode materials. The further improvement of these materials should focus on not only using conventional doping, substitution, and coating methods to stabilize against oxygen release, but also effectively minimizing the mechanical consequence of oxygen release under various scenarios of battery usage, such as high voltages and/or high temperature.

Experimental Section. Synthesis Method. $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ was synthesized using a coprecipitation method with $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.99%), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Sigma-Aldrich, 99%), and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich, 99%) as the raw materials. The transition metal solution (0.04 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.04 M $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, and 0.02 M $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in 100 mL of H_2O), starting solution (40 mL of NaOH and $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous solution with a molar ratio $\text{NaOH}/\text{NH}_3 = 1.2$, pH value was adjusted to 10.5), and base solution (100 mL of NaOH and $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous solution with a molar ratio $\text{NaOH}/\text{NH}_3 = 1.2$) were made and separately stored in Kimble bottles. The transition metal solution and base solution were simultaneously pumped into the starting solution at a drop rate of ~ 2 mL/min with continuous stirring at 50°C under the N_2 protection. The drop rate of the base solution was frequently tuned to keep the pH at 10.5 ± 0.2 . The precipitate was collected, washed, and filtrated with deionized (DI) water and dried in vacuum oven overnight at 100°C . The dried precursor was then mixed with LiOH thoroughly and calcined under air flow (2 L/min) at 725°C for 6 h to obtain the final $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ powder. Subsequently, we used $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ to obtain delithiated $\text{Li}_{1-x}\text{Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ particles by chemical delithiation. Briefly, 1 g of $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ powder was dispersed in 0.11 M NO_2BF_4 (Acros Organic, 97%) dissolved in acetonitrile (CH_3CN , Fisher Chemical, 99.9%), and continuously stirred for 24 h in an Ar-filled glovebox ($\text{H}_2\text{O} < 0.5$ ppm, $\text{O}_2 < 0.5$ ppm) at room temperature. Then, the delithiated powder was collected and washed three times using acetonitrile. Finally, the $\text{Li}_{1-x}\text{Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ product was dried overnight. The delithiated samples were handled with caution to limit the exposure to the ambient air, which was shown to be sufficient to protect the surface chemistry of delithiated NMCs.⁴¹

Materials Characterization. XRD was performed at beamline 11-3 of SSRL. Transmission XRD ring patterns were detected. LaB_6 patterns were collected as reference data for calibration, and exposure time was only 0.5 s for the samples to avoid any saturation. Scanning electron microscopy (SEM) was performed on a JEOL JSM-7000F instrument with a Thermo Scientific EDS (energy dispersive X-ray spectroscopy) detector. Hard X-ray Raman scattering (XRS) measurements were performed at beamline 6-2B at SSRL. The spectra were recorded with samples kept in helium atmosphere, and each spectrum was a bandwidth of 0.55 eV; the incident photon energy was selected with a double-crystal average of multiple spectra collected over the 2 h period. The X-ray Raman signals were collected with Si-660 reflection of the 40-crystal XRS spectrometer at 9694.8 eV with a monochromator Si (311) around 10.3 keV to have the Raman offset corresponding to Mn L2,3-edges, Co L2,3-edges, and Ni L2,3-edges. Soft XAS measurements were performed on the 31-pole wiggler beamline 10-1 at Stanford Synchrotron Radiation Lightsource (SSRL)

516 using a ring current of 350 mA and a 1000 L/mm spherical
517 grating monochromator with 20 μm entrance and exit slits,
518 providing $\sim 10^{11}$ ph/s at 0.2 eV resolution in a 1 mm² beam
519 spot. Data were acquired under ultrahigh vacuum (10^{-9} Torr)
520 in a single load at room temperature using total electron yield
521 (TEY), where the sample drain current was collected, and in
522 the fluorescence yield (FY), where a silicon diode (IRD AXUV-
523 100) was used to collect the FY positioned near the sample
524 surface. All spectra were normalized by the current from freshly
525 evaporated gold on a fine grid positioned upstream of the main
526 chamber. The transmission X-ray tomography was performed
527 at beamline 6-2c at SSRL. An in-house developed software
528 package known as TXM-Wizard was used for the analysis of all
529 the tomography results.

530 *In Situ Heating.* Delithiated NMC particles were loaded on a
531 silicon nitride passivated silicon chip. The particles were
532 subsequently heated at 235 °C by a local Joule heating element
533 integrated on the silicon chip. All *in situ* S/TEM images and
534 movies were recorded on a FEI Environmental Titan
535 instrument operated at 300 keV. A Denssolution MEMS
536 heating holder (Model Wildfire S3) was used to heat the
537 particles. Helium was flown through the objective volume in
538 the environmental TEM, and a pressure of 0.2 mbar in the
539 sample area was maintained during the *in situ* heating
540 experiment. *Ex situ* TEM images and electron energy loss
541 spectra (EELS) were acquired on a JEOL 2100 S/TEM
542 instrument operated at 200 keV.

543 *Methodology of Finite Element Modeling.* We performed
544 finite element simulations (FEM) to understand the stress and
545 intergranular/intragranular cracks in NMC under thermal
546 abuse conditions. Delithiated NMC is subject to the strain
547 field, $\epsilon = \epsilon_{\text{TE}} + \epsilon_{\text{PT}} + \epsilon_{\text{OR}}$, where ϵ_{TE} , ϵ_{PT} , and ϵ_{OR} represent the
548 strains induced by thermal expansion, phase transition, and
549 oxygen release, respectively. ϵ_{TE} is considerably smaller than the
550 strains induced by phase transition and oxygen release.^{55,57}

551 Here we have ignored ϵ_{TE} in the modeling. The phase-
552 transition strain ϵ_{PT} is highly anisotropic. A prior study using *in*
553 *situ* XRD measurements determined that the lattice constants
554 along *a* and *c* directions increased by 4.48% and 0.74% upon
555 the phase transition from the layered to spinel-like/rocksalt
556 structures, resulting in a triaxial strain field: $\epsilon_a = \epsilon_b = 4.48\%$ and
557 $\epsilon_c = 0.74\%$.⁵⁵ For the oxygen release induced strain ϵ_{OR} , it is
558 assumed to be proportional to the normalized oxygen vacancy
559 concentration \bar{c}_v , $\epsilon_{\text{OR}} = 1/3\beta_c\bar{c}_v$, where β_c represents the
560 chemical expansivity dictating the volumetric change caused by
561 the formation of oxygen vacancy.⁵⁷ \bar{c}_v is related with the
562 normalized oxygen concentration \bar{c}_O , $\bar{c}_v = 1 - \bar{c}_O$, where \bar{c}_O is
563 defined as the ratio of the oxygen concentration c_O upon
564 oxygen release to the initial value $(c_O)_{\text{in}}$, $\bar{c}_O = c_O/(c_O)_{\text{in}}$. The
565 kinetics of oxygen release is assumed to follow Fick's law, $dc_O/dt = D_O\nabla^2c_O$, where D_O is the diffusivity of oxygen in NMC.
566 Similar to Li diffusion in the layered structure, oxygen diffusion
567 is dependent on orientation where the release rate within the
568 *a-b* plane is faster than that along the *c* direction.⁴ The strain
569 fields ϵ_{PT} and ϵ_{OR} serve as the input of the FEM model, and the
570 stress field is solved within the framework of elasticity theory.
571 The cohesive zone model is employed to simulate the
572 nucleation and propagation of intergranular/intragranular
573 cracks.³⁸ When the energy release rate reaches the fracture
574 toughness of the grain boundaries or the interior grains,
575 intergranular or intragranular cracks initiate and propagate. All
576 the parameters used in simulation are listed in Table S1.

■ ASSOCIATED CONTENT

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📄 Supporting Information

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The Supporting Information is available free of charge on the
ACS Publications website at DOI: 10.1021/acs.nano-
lett.8b01036.

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Additional data and figures including STEM images, STEM
TEM images, soft XAS spectra, transition X-ray
tomography, and large-area EELS (PDF)

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Movie S1: representative accelerated STEM results
(MPG)

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Movie S2: particle at different cross sections through the
3D STEM tomography (MPG)

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Author Contributions

599

L.M., M.M.D., H.L.X., and F.L. participated in conceiving and
designing the project. L.M., R.L., L.H., S.X., D.S., J.D.S.,
T.C.W., D.N., Y.L., H.L.X., and F.L. all participated in
performing experiments. R.X. and K.Z. performed and wrote
finite element modeling. L.M. and F.L. wrote the manuscript
with help from all coauthors. F.L. directed the project.

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Notes

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The authors declare no competing financial interest.

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