Journal of Materials Chemistry A

REVIEW

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Cite this: J. Mater. Chem. A, 2018, 6, 21859

Received 17th July 2018 Accepted 19th September 2018

DOI: 10.1039/c8ta06875e

rsc li/materials-a

Introduction 1.

In order to ensure a green and pollution-free future, harvesting energy from sustainable resources and shifting from gasolinepowered vehicles to electric vehicles (EVs)¹ are of prime

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Chemomechanical behaviors of layered cathode materials in alkali metal ion batteries

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Layered cathode materials (LCMs), because of their high energy density and relatively stable performance, represent an important class of cathode materials for alkali metal ion (e.g., Li⁺ and Na⁺) batteries. Chemomechanical behaviors of LCMs, which affect battery performance dramatically, have drawn extensive attention in recent years. Most chemomechanical processes have some common chemical and structural origins that are at the center of materials chemistry, for example, defects and local bonding environments in the solid state. In this review, we first discuss the chemomechanical breakdown of LCMs by introducing their categories and negative effects on the battery performance. We then systematically analyze factors that govern the initiation and propagation of chemomechanical breakdown and summarize their formation mechanisms. Strategies that can enhance the chemomechanical properties of LCMs or reduce the destructive effects of chemomechanical breakdown are then discussed. Finally, light is shed on the new state-of-the-art techniques that have been applied to study chemomechanical breakdown. This review virtually includes most aspects of the chemomechanical behaviors of LCMs and provides some insights into the important chemical motifs that determine the chemomechanical properties. Therefore, we believe that advanced design protocols of LCMs can be developed to effectively address the chemomechanical breakdown issue of LCMs.

> importance. To achieve these two goals, it is crucial to develop grid-scale energy storage systems and EVs.² A promising energy storage candidate for grids and EVs is alkali metal ion batteries (e.g., lithium-ion batteries, LIBs). LIBs have been widely used in portable electronics because of their high energy density, high power density, superior safety features, and long cycle life.³ However, LIBs cannot satisfy the increasing performance requirements for modern portable electronics, EVs, and gridscale energy storage systems. We have witnessed impressive progress in integrated circuits (ICs) in the past 50 years, which

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has almost followed Moore's law⁴ which states that the number of transistors per square inch doubles every 18 months. More transistors mean faster processing capability and consequently more energy consumption. However, the performance of the power provider (LIBs) is lagging far behind. We also witnessed exciting progress in harvesting different forms of sustainable energy, such as wind energy,^{5,6} solar energy,^{7,8} hydropower energy,⁹ biomass energy,^{10,11} and marine energy.¹² Nevertheless, the aforementioned sustainable energy resources have the same intrinsic drawbacks: intermittency and unpredictable fluctuations. Integrating these fluctuating green energy resources is a huge challenge to the modern grid.¹³ Storing renewable energy is therefore vital for practical applications.¹⁴

To further enhance the performance of LIBs, we need a better understanding of their fading mechanisms. Chemomechanical breakdown (*i.e.*, formation of cracks), one of the main fading mechanisms of LIBs, has been widely observed in the anode, solid–electrolyte interphase (SEI), and cathode. Strategies to inhibit chemomechanical breakdown of anode



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To improve the volumetric energy density and stability of LCMs (*e.g.*, LiNi_xMn_yCo_{1-x-y}O₂, NMC), most studies aim to form micron-sized spherical polycrystalline particles consisting of nano-sized single crystals.^{38,39,41-43} In addition, great effort has been made to push the charge cut-off voltage higher than 4.5 V (all voltages in this paper are against Li/Li⁺) to reach the capacity that is close to the theoretical limitation.^{38,44} Therefore, the chemomechanical breakdown of LCM polycrystalline particles can occur due to the random orientation of the single crystals, anisotropic volume expansion/contraction, electrolyte infiltration, lattice oxygen release, and heterogeneous phase transformations. Chemomechanical breakdown of the cathode leads to the detachment of active particles from the nearby active particles, conductive carbon matrices, and current collector.



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This detachment can lead to reduced electronic conductivity40 and loss of effective active particles.45 Moreover, cracked cathode particles have a larger surface area because the cracks expose the intact bulk.41 The increased surface area and electrolyte penetration result in more undesired cathode-electrolyte side reactions^{3,34} and accelerated transition metal dissolution.46,47 Thus, the formation of cracks imposes negative effects on the battery performance. The formation of cracks is governed by different factors, and here we categorize these factors as intrinsic and extrinsic factors. The intrinsic factors are related to the cathode itself, such as the cathode composition41,44 and particle size.48,49 The extrinsic factors are associated with charging and discharging conditions, and examples are depth of charge/discharge,50 cycling-rate,51,52 and cycle number.40,53 Cracking has been intensively observed, yet its formation mechanisms have not been completely understood. Evolution of the crystal structure can introduce volume change and subsequent microstrain in the particles,⁵⁴ and when the strain reaches a certain level, it will be released through the formation of cracks. Defects (e.g., dislocations) inside the primary particles can propagate and lead to the formation of intragranular cracks.38 Moreover, release of lattice oxygen reduces the stability of the cathode and is partially responsible for the formation of intragranular and intergranular cracks.35,36 Equipped with the knowledge of crack formation, some strategies have been designed to mitigate cracking or reduce the negative effects of cracks. Among those strategies, surface engineering has been shown to be the most common and effective one.55 Other strategies, such as grain engineering,56 elemental substitution,57 pre-cycling treatment,58,59 reducing particle size,60 and electrolyte additives,61 are also covered in this review. Chemomechanical breakdown of LCMs for sodiumion batteries (SIBs) is compared with that in LIBs.62,63 Finally, some recently developed analytical techniques49,64,65 are reviewed to understand the methodology for studying the chemomechanical properties of LCMs. The purpose of this review is to summarize the recent progress in characterizing, understanding, and modifying the chemomechanical properties of LCMs, with an emphasis on LCMs for LIBs.

2. Categories of cracks and their impact on battery performance

The LCMs are designed to have a spherical morphology for the relatively small surface area. Secondary particles of LCMs consist of densely packed single crystals (*i.e.* primary particles) with mostly random orientations (Fig. $1(a)^{39}$). An exception is that LiCoO₂ (LCO), one of the LCMs, has large single crystals.⁶⁶ Such a structural design can enhance its volumetric density and alleviate cathode–electrolyte side reactions because of the relatively small surface area. However, this structural design has an unresolved problem: during the charging and discharging process, formation of cracks can occur inside and between primary particles, which can then increase the surface area of the cathode and induce more side reactions relative to those intact particles.

Based on the physical location, cracks can be divided into two main categories: intragranular cracks and intergranular cracks; the former occur within the primary particles,38,41-43 whereas the latter occur between the primary particles (usually along grain boundaries).³⁹ Intragranular cracks are usually caused by the loss of several transition metal layers.³⁸ The dark straight lines, pointed by the yellow arrows in Fig. 1(b),³⁸ are intragranular cracks in a LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC333) material. It is evident that intragranular cracks are inside a primary particle, and their length ranges from tens to hundreds of nanometers. Intragranular cracks are widely observed in LCMs, such as NMC333,38 LCO,67 LiNi0.6Mn0.2C00.2O2 (NMC622),68 and even in olivine-type cathode materials such as LiFePO4 (LFP).69 Although it is challenging to quantify the negative impact of intragranular cracks, it ultimately leads to the formation of large cracks that act similar to intergranular cracks. The density of intragranular cracks is usually orders of magnitude higher than that of intergranular cracks.⁷⁰ Intergranular cracks form between the primary particles and usually along grain boundaries.35 Fig. 1(c)41 shows the intergranular cracks (irregular void regions inside the secondary particle) in a Ni-rich NMC material. Intergranular cracks have a much larger size compared to intragranular cracks. Intergranular cracks are also widely reported in LCMs, for example, LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA),⁴⁰ LiNiO₂ (LNO),⁵⁰ NMC333,⁷¹ and olivine-type LFP.^{72,73}

The formation of intragranular and intergranular cracks is inevitable in most LCMs, and their occurrence commonly accompanies decreased electrochemical performance. Four main negative impacts are included in this review (Fig. 2): poor electronic conductivity, loss of active material, more severe cathode–electrolyte side reactions, and dissolution of transition metals. These four main negative effects are not independent of each other, and the electrochemical performances of LIBs are compromised by the synergistic effect of these four negative impacts.

Poor electronic conductivity

During the charging process, electrons in the cathode material move across primary cathode particles and then travel to the anode through the external circuit. Intergranular cracks in cathode particles can lead to the detachment of the active material from the nearby active material, conductive carbon black matrices, and current collector, which is responsible for the inferior electronic conductivity. This reduced electronic conductivity leads to a dramatic increment of $R_{\rm ct}$ (charge-transfer kinetic resistance), which is considered as an important factor for significant capacity drop.^{40,74,75}

The inferior electronic conductivity can further lead to stateof-charge (SOC) heterogeneity in individual particles. SOC heterogeneity means the non-uniform oxidation state distribution of a transition metal (*e.g.*, Ni),⁷⁶ which accounts for accelerated crack formation.^{49,77} Liquid electrolytes are a good Li ion conductor but not an electron conductor, while solid cathode particles can conduct both electrons and Li ions. This means that Li ions can diffuse through the cathode and electrolyte, while electrons can only be conducted through the solid



Fig. 1 (a) Illustration of primary and secondary particles: scanning electron microscopy (SEM) image of uncycled NCA primary and secondary particles.³⁹ (b) An example of intragranular cracks: low magnification high-angle annular dark-field (HAADF) image of NMC333 (after 100 cycles at 4.7 V cut-off voltage), showing the intragranular cracks (yellow arrows) inside the primary particles.³⁸ (c) An example of intergranular cracks: cross-sectional SEM image of the $Li_{1-\delta}Ni_{0.95}Co_yMn_{0.05-y}O_2$ cathode particle (first fully charged at 4.3 V cut-off voltage).⁴¹ Used with permission from ref. 38, 39 and 41.

cathode. Before cracking, the Li ions and electrons at the same spot share the same geometrically optimal pathway (Fig. 3(a) green lines). Therefore, there is no path length difference between the Li ions and electrons at the same physical site. In contrast, cracking and electrolyte infiltration induce the path length difference between the Li ions and electrons. During the charging process, the Li ions diffuse to the surface of the solid cathode and are then conducted through the liquid electrolyte, which possesses higher Li ion conductivity than the solid cathode. When the electrolyte penetrates the cracked cathode particles, it reduces the path length of Li ions that are inside the particles (Fig. 3(a) blue lines). Meanwhile, the cracks generally increase the path length of electrons. Cracks are physical barriers to electrons, which means the electrons need to detour and travel longer distances to reach the surface (Fig. 3(a) red lines). The path length difference between the electrons and Li ions at different spots can be calculated, and the results are shown in Fig. 3(b). Intergranular cracks lead to different degrees of path length difference based on the geometry of cracks and electrolyte infiltration effect. Moreover, the difference in the diffusion time of Li ions and electrons leads to charge

heterogeneity at the secondary particle level. The electrons in the cathode particle need to move to the surface during the charging process, and after crack formation (Fig. 3(c)), different regions of the surface have different electron traffic because of the electron detour effect (Fig. 3(d)). Recently, Tian *et al.* observed charge heterogeneity for NMC622 particles after electrochemical delithiation (Fig. 3(e)).⁷⁶ The inhomogeneous Ni oxidation states were partially due to the disruption of electronic wiring and subsequent particle isolation.

Loss of active material

Disconnection in LCMs, induced by intergranular cracks, can lead to an etched surface after cycling (Fig. 4(a) and (b)), and part of this etched surface will further separate from the bulk region and form fragmented pieces (Fig. 4(c)). These fragmented pieces are "dead regions" of the cathode for two reasons. One is that once the fragmented pieces detach from the bulk region, the electrons in these fragmented pieces cannot reach the surrounding conductive matrices. The fragmented pieces thus cannot contribute to the electrochemical



Fig. 2 Schematic representation of the four negative impacts induced by intragranular and intergranular cracks. The irregular yellow regions represent primary particles and the red lines represent grain boundaries. Primary particles have random orientations and they pack tightly to form the secondary particles. The green stripes inside the primary particles are intragranular cracks, while the green gaps between primary particles are intergranular cracks.

reaction anymore. The other reason is that Mn ions in the fragmented pieces are permanently reduced from Mn^{4+} to Mn^{2+} , most likely in forms of redox inactive rock-salt phases. Electron energy loss spectroscopy (EELS) spectra (Fig. 4(c)–(e)) indeed show that Mn ions in the fragmented pieces were Mn^{2+} , while the Mn ions in the bulk were Mn^{4+} . The "dead regions" cannot intercalate or de-intercalate Li ions anymore, which is partially responsible for capacity fading.

Accelerated cathode-electrolyte side reactions

Secondary particles of LCMs are designed to have a spherical morphology to reduce their specific surface area. Intergranular cracks can produce fresh surfaces and expose the formerly intact grain boundaries to the liquid electrolyte. The fresh surfaces can react with the liquid electrolyte and form more surface reconstruction layers. Surface reconstruction layers are electrochemically inactive with relatively inferior ion conductivity, which partially accounts for the resistance buildup and capacity fading in LIBs.^{40,41} Surface reconstruction involves the structural change from $aR\bar{3}m$ layered structure to a $Fm\bar{3}m$ rocksalt (Fig. 5), and it has been intensively observed for LCMs,^{33,78–80} including stoichiometric layered materials and Li/Mn-rich layered oxides. The degraded surface layer forms instantly after the cathode particles are soaked in the liquid electrolyte, and its

thickness can increase after cycling. This proves that the surface reconstruction process involves both cathode–electrolyte reactivity and electrochemical activation.³³ Moreover, the surface reconstruction predominantly occurs along the Li-diffusion direction, and examples include $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ (NMC442) (Fig. 5(a))³³ and Li/Mn-rich layered oxides (Fig. 5(b)).⁷⁸ The surface reconstruction is mainly induced by lattice oxygen release and the preferential migration of Mn and Ni ions.⁷⁹ It was observed that the removal of Li ions accompanies the loss of lattice oxygen ions at the surface. As a result, some surface transition metal ions only coordinate with five oxygen ions, and the destabilized transition metals will then move to the empty Li sites and form the rock-salt structure. When Mn ions migrate to the bulk, the Mn-to-Ni ratio increases from the surface to the bulk, as shown in Fig. 5(c).⁷⁹

Dissolution of transition metals

The dissolution of transition metals, such as Ni, Co, and Mn, is more severe after chemomechanical breakdown. Among the three aforementioned transition metals, the dissolution of Mn ions was reported to be the easiest^{46,47} and it can occur through two possible mechanisms. The first mechanism is the Mn³⁺ disproportionation reaction according to the 2Mn³⁺ \rightarrow Mn²⁺+ Mn⁴⁺ route.^{81,82} The second mechanism is the HF attack on the



Fig. 3 (a and b) Simulation of the electrolyte infiltration effect: (a) schematic representation of the diffusion pathways for electrons and Li ions before the crack formation (green lines), electrons after crack formation (red lines), and Li ions after crack formation (blue lines). The gray domains are cathode materials, the void regions between cathode materials are intergranular cracks, and the cyan background is the liquid electrolyte. (b) Color map showing the path length difference between Li ions and electrons induced by cracking and electrolyte infiltration. The path length difference is calculated by subtracting the path length of Li ions from that of electrons at the same spot. Blue represents a small difference and red means a large difference. (c) 3D rendering of the NMC622 particle that has been cycled 50 times at 10C. (d) Traffic load (the number of electrons passing through a specific surface area) map of the particle in (c).⁴⁹ (e) Color mapping of the Ni oxidation state heterogeneity of the electrochemically charged NMC622 electrode, where blue represents a low oxidation state and red indicates a high oxidation state.⁷⁶ Used with permission from ref. 49 and 76.

cathode.^{83,84} LiPF₆, a common component of the liquid electrolyte, decomposes easily as LiPF₆ \rightarrow LiF + PF₅. With traces of water, PF₅ can further decompose as PF₅ + H₂O \rightarrow 2HF + POF₃.⁸⁴ HF can then react with the cathode, leading to the dissolution of transition metals. Moreover, H₂O is another product from the cathode–HF reaction, and H₂O promotes the decomposition of PF₅ and produces more HF, which makes the transition metal dissolution reaction auto-catalytic.⁸⁵ The dissolution of Mn ions has two main negative impacts. Mn ions dissolved in the electrolyte can re-deposit on the cathode surface,⁸⁶ which induces a resistive layer for electrons and Li ions. The dissolved Mn ions can also migrate to the anode surface through the electrolyte⁸⁷ and interrupt the formation of the SEI layer.⁸⁸ Transition metals deposited on the anode work as catalysts for the decomposition of SEI components, which

leads to the formation of an inactive layer on the anode surface and cracks in the SEI layer.⁸⁸ The decomposition of $(CH_2-OCO_2Li)_2$ (one of the SEI components) promotes the formation of Li_2CO_3 , which can react with $LiPF_6$ to produce LiF and CO_2 .⁸⁹ Moreover, the decomposition of $(CH_2OCO_2Li)_2$ can induce some cracks in the SEI, and these cracks contribute to more SEI formation. As a result, the dissolution of transition metals interrupts the formation of the SEI layer and induces more SEI formation, which leads to decreased electrochemical performance.

The dissolution of Co ions is widely observed in Co-containing cathode materials,^{57,90} though it is not dominant. Moreover, the dissolution of Ni ions from the surface usually accompanies the surface transformation from a layered structure to a spinel and/or rock-salt structure. Although the



Fig. 4 (a–c) Etched surface of the $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ cathode after cycling. (a) Overview image of the surface after cycling. (b) Zoomed-in image of the white rectangular region in (a). (c) Overview image of the fragmented pieces and cycled bulk of the cathode. (d–f) EELS results of the cycled bulk (blue) and fragmented pieces (red): (d) O K, MnL, and NiL edges, (e) MnL edge, and (f) MnM and Li K edges.⁴⁵ Used with permission from ref. 45.

dissolution of Ni is not dominant, it can be accelerated with a high Ni-content, high cut-off voltage, and elevated temperature.³⁷ An example is that the degree of Ni dissolution in $LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ is an order of magnitude higher than that in NMC622.⁴⁴ Interestingly, the dissolution of Co and Mn ions is also more severe in high Ni-content samples. Even though the Co and the Mn concentration in $LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ is only one-fourth of that in NMC622,⁴⁴ the dissolution of Co and Mn ions is much more obvious in the former. The possible reason is that $LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ has more cracks, which provide channels for electrolyte infiltration and induce more cathode– electrolyte reactions.

3. Factors affecting the crack formation and crack formation mechanisms

Despite how intriguing the phenomenon of crack formation can be, there are a limited number of reports on the formation mechanisms of cracks. The factors affecting the crack formation can be traced down to intrinsic and extrinsic factors. Intrinsic factors are mainly related to the properties of cathode particles. To the best of our knowledge, the Ni-content and particle size are reported to affect the formation of cracks. Extrinsic factors can be attributed to charging and discharging conditions, such as the state of charge, cycling rate, and cycle number. Intrinsic and extrinsic factors affect crack formation mainly based on three different mechanisms: evolution of the crystal structure, propagation of defects (*e.g.*, dislocations), and lattice oxygen release.

Intrinsic factors

Ni-content. Undesired side reactions, such as surface reconstruction and transition metal dissolution, are more severe in Ni-rich materials (LiNi_xMn_yCo_{1-x-y}O₂, x > 0.8). Ni-rich materials41,91-94 have more severe phase transition near the end of charge, which leads to a higher extent of anisotropic volume change and produces a more freshly exposed surface area. The severe anisotropic volume change, however, can be suppressed when x (the Ni-content) is less than 0.8 (Fig. 6(a)). At the beginning of the charging process, the *c* axis of samples with different Ni-contents expands to the same length. However, near the end of charging, the c axis of NMC622 shrinks by only 2.6%, while $\text{LiNi}_{0.95}\text{Co}_{0.025}\text{Mn}_{0.025}\text{O}_2$ shrinks by 6.9% in the c axis (Fig. 6(b)). This dramatic difference accounts for the larger size and higher density of cracks in Ni-rich samples. The cracks in the Ni-rich sample, indicated by the red lines in Fig. 6(a), provide more channels for electrolyte infiltration. Fresh cathode surfaces can then react with the electrolyte and form NiO-like layers at the surface and in the interior of cathode particles. The NiO-like layer can impede Li ion diffusion and lead to impedance increment (Fig. 6(c)). A higher Ni-content can enhance the initial discharge capacity; however, it deteriorates the stability of the NMC material, as shown in Fig. 6(d). NMC622 had an





Fig. 5 (a) Observation of surface reconstruction layers of NMC442 particles (after 1 cycle, 2.0-4.7 V) with annular dark-field scanning transmission electron microscopy (ADF-STEM). The scale bar is 2 nm.³³ (b) The surface reconstruction layers in cycled Li/Mn-rich Li[Ni_{1/5}Li_{1/5}Mn_{3/5}] O_2 .⁷⁸ (c) The surface reconstruction layers, chemical map, and evolution of the Mn and Ni atomic concentration in Li/Mn-rich Li_{1.2}Mn_{0.61}-Ni_{0.18}Mg_{0.01}O₂ (after 50 cycles under C/2).⁷⁹ Used with permission from ref. 33, 78 and 79.

initial capacity of around 180 mAhg⁻¹ at 0.5C, and the capacity retention was 96.5% after 100 cycles, whereas the initial capacity of LNO was around 230 mAhg⁻¹ at 0.5C and the capacity retention was only 74.9% after 100 cycles.

In addition to more crack formation, a higher Ni-content also leads to thicker surface degradation layers. A comparison between NMC622 and $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ (ref. 44) depicts that increasing the Ni-content in NMC leads to a thicker NiOlike surface degradation layer. Fig. 7(a) and (b) show the transmission electron microscopy (TEM) images of NMC622 with a cut-off voltage of 4.3 V and 4.5 V, respectively. The thickness of the surface degradation layer is about 3 nm. By increasing the Ni-content to 0.9, the thickness of the surface degradation layer increases and a thin amorphous layer also forms above the NiO-like rock-salt structure layer. As seen in Fig. 7(c) and (d), the surface degradation layer is about 5 nm thick for $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ with a cut-off voltage of 4.3 V and 4.5 V, respectively. The amorphous layer is formed by the release of oxygen.

Particle size. Particle size, including primary and secondary particle sizes, is thought to be another intrinsic factor that affects the formation of cracks. Our recent study⁴⁹ shows that

the size of secondary particles positively correlates with the degree of cracking, as attested by the transmission X-ray microscopy (TXM) data (Fig. 8(a) and (b)). Obviously small particles are more robust against crack formation; however, a nano-sized secondary particle design cannot be adopted for practical cathodes, because nano-sized secondary particles have inferior packing density48 and more severe cathode-electrolyte reactions. The reason why larger secondary particles lead to more cracks has not been understood yet. The consensus among materials scientists is that micro-fractures in ceramics can be suppressed if the grain size is below a material-specific size.95 With an analytical micromechanical model, Chiang60 and coworkers showed that when the primary particle size is smaller than some critical value, grain boundary micro-fracture formation in LCMs would be suppressed. Fig. 8(c) shows the critical sizes for LCO, NCA, and NMC, below which microfractures will not grow.

Extrinsic factors

State of charge. During the charging process, Li ions deintercalate from the cathode and intercalate into the anode.



Fig. 6 (a) Schematic figure showing the capacity fading mechanism of Ni-rich NMC cathodes. A higher Ni-content results in a higher extent of anisotropic volume change and subsequently more cracks in the cathode particles. More and larger cracks provide more channels for electrolyte infiltration, which leads to more severe surface degradation. Evolution of the (b) *c*-axis lattice parameter, (c) charge transfer resistance, and (d) discharge capacity of Ni-rich NMC materials with different Ni-contents (x = 0.6, 0.8, 0.9, 0.95, and 1).⁴¹ Used with permission from ref. 41.

Charging the cathode to a higher voltage can extract more Li ions from the cathode and deliver a higher discharge capacity.⁹⁶ However, a higher cut-off voltage correlates with more phase transformation processes and subsequently more crack formation. The phase transformation process will be discussed in detail later.

LNO particles remain intact when they are cycled at a low cutoff voltage (4.1 V), as shown in Fig. 9(a) and (d). When increasing the cut-off voltage to 4.2 V, crack formation becomes obvious (Fig. 9(b) and (e)). Moreover, if the cut-off voltage reaches 4.3 V, the crack formation increases dramatically, as seen in Fig. 9(c) and (f).⁵⁰ The underlying mechanism for such an observation is the phase transformation process at a high cutoff voltage, which can generate mechanical strains and accelerate the formation of micro-cracks.⁵⁷The dQ/dVplots of the samples with different cut-off voltages are shown in Fig. 9(g)–(i). The repeated H2 \rightarrow H3 phase transition^{44,97} at 4.15 V is considered as the primary factor that causes crack formation. Capacity fading can be mitigated by limiting the cut-off voltage of LNO to 4.1 V. In addition, a higher cut-off voltage leads to more severe crack formation which is also observed in NMC materials.^{75,98}

Cycling-rate. Fast charging and discharging capability is an important parameter for practical batteries, especially for those designed for EVs. Fast charging and discharging is usually correlated with more severe crack formation in the cathode, as observed in NCA⁵¹ and NMC⁵² materials, which leads to decreased electrochemical performance. The intrinsic reason may be that fast charging and discharging processes accompany a rapid volume change, which produces a strain that cannot be accommodated accordingly in a considerably short period. Our recent study⁴⁹ showed that a higher cycling rate leads to a dramatic increment of crack formation at the secondary particle level.

However, some researchers hold an opposite opinion that crack formation is independent of fast charging and discharging. Zhao *et al.*⁷⁵ argued that the mechanical disintegration caused by fast charging was not obvious. They pointed out that a higher cycling-rate could limit the total amount of Li ions inserted or extracted from the layered structure, which would



Fig. 7 Comparison of surface degradation layers in NMC622 and $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$ at different cut-off voltages based on TEM images: TEM images of NMC622 charged to (a) 4.3 V and (b) 4.5 V. TEM images and Fourier transform images of $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$ charged to (c) 4.3 V and 4.5 V.⁴⁴ Used with permission from ref. 44.



Fig. 8 (a) Visualization of crack formation in NMC secondary particles of different sizes. All the particles were cycled at 10C 50 times. (b) Quantification of the porosity and the specific crack surface area of the particles in (a).⁴⁹ (c) SOC-dependent critical sizes for selected LCMs.⁶⁰ Used with permission from ref. 49 and 60.



Fig. 9 Cross-sectional SEM images of the first charged LNO cathode at (a and d) 4.1 V, (b and e) 4.2 V, and (c and f) 4.3 V. The dQ/dV curves from the initial charge and discharge curves at upper cutoff voltages of (g) 4.1 V, (h) 4.2 V, and (i) 4.3 V.⁵⁰ Used with permission from ref. 50.

reduce the volumetric change of the cathode and thus lower the disintegration extent of the secondary particles. Their observation of reduced $R_{\rm SEI}$ (Li ion transport resistance through the SEI) and $R_{\rm ct}$ for fast charging and discharging samples proved that a less fresh surface was produced because of the lower extent of crack formation. Another example is that for NMC333, 0.1C and 1C made no difference to crack formation when the cell was cycled at a low cut-off voltage.³⁸ Furthermore, *in situ* acoustic emission experiments⁶⁰ showed that the C-rate independent crack formation is also valid in LCO. Therefore, these contradicting studies signify the need for more investigations to better understand the relationship between fast charging and crack formation.

Cycle numbers. It is believed that chemomechanical breakdown occurs only after long term cycling.^{99,100} However, researchers have observed crack formation even after the first cycle.^{40,53} The fracture and fragmentation evolutions in NCA materials⁴⁰ were successfully characterized using the SEMfocused ion beam (SEM-FIB) snapshot approach. Fig. 10(a) to (d) show the same particle in the as-prepared conditions and after the first, second, and third cycle. It is evident that the asprepared sample had an intact secondary particle, and the crack formation and intergrain separation occurred after the first cycle and increased as a function of cycle number. Furthermore, the elastic modulus and hardness of NMC materials98 showed the most dramatic reduction after the first cycle, and then they decreased gradually as a function of cycle number. This means that most chemomechanical breakdown occurred during the first cycle, and afterwards cracks grew at a much slower speed. The mechanism behind such an observation has not been proposed yet. Here, we propose a possible mechanism called the "positive feedback effect". During the charging and discharging process, charge heterogeneity is induced by crack formation, as shown in Fig. 3(d) and (e). This charge



Fig. 10 (a–d) The evolution of particle fracture and fragmentation as a function of cycle number: these SEM-FIB snapshot images show the same particle in the (a) as-prepared condition and after the (b) first, (c) second, and (d) third cycles.⁴⁰ (e) The evolution of crack length for four independent cracks as a function of time under thermal abuse conditions.³⁵ (f) Cumulative acoustic counts for sintered and thick composite pellet LCO electrodes during the first charge at a C/50 rate.¹⁰¹ Used with permission from ref. 35 and 40 and 101.

heterogeneity, in turn, induces more micro-strain, which can accelerate the crack formation process. Overall, more cracks promote a higher extent of charge heterogeneity and a higher extent of charge heterogeneity induces more micro-strain, which can accelerate the crack formation process. This positive feedback theory can explain that at the beginning of the crack formation process, the strain accumulated, and when the strain reached a specific level, the number of cracks would increase dramatically. Fig. 10(e) shows that the length of cracks increased dramatically in the beginning and gradually afterwards. The former result is consistent with Carter's acoustic emission experiment (Fig. 10(f)),60 which proved that crack formation increased dramatically in the middle of the first charge cycle. The acoustic emission experiment also showed that crack formation was highly concentrated in the first charge cycle. The possible reason is that after the drastic crack formation process, a large volume of cracks can accommodate the volume change of the cathodes. A complete understanding of the microstructural evolution at the early stage needs further investigation.

Crack formation mechanisms

Evolution of crystal structures. During the electrochemical cycling processes, the lattice structure of LCMs experiences periodic changes, ^{54,92,102,103} which lead to micro-strain accumulation¹⁰⁴ and subsequent crack formation. The *in situ* synchrotron X-ray diffraction (XRD) patterns of the NMC622 material in Fig. 11(a) show that the peak positions changed periodically and had high reversibility. The corresponding lattice parameters and unit cell volumes are shown in Fig. 11(b) and (c), respectively. For the H1 phase, the *a*, *b*, and *c* lattice parameters showed negligible changes. For the H2 phase, as Li ions de-



Fig. 11 (a) In situ synchrotron XRD patterns of NMC622 (cycled at C/10 between 2.5 and 4.7 V) showing the periodic changes of the crystal structure. The evolution of (b) a and c-axis parameters and (c) the unit cell volume change of NMC as a function of charge/discharge depth during the first cycle.⁵⁴ Used with permission from ref. 54.

intercalated from the structure, the c lattice parameter first increased while the a/b lattice parameter decreased. With more Li ions removed from the lattice (cut-off voltage higher than 4.2 V), the *c* axis contracted dramatically while the a/b lattice parameter increased slightly. The calculated unit volumes are shown in Fig. 11(c), and the volume change is about 4%, which proves that the bulk crystal structure is stable during electrochemical cycling processes. However, in the vicinity of the particle surface, after the removal of surface Li ions, transition metal ions could move to the vacant Li sites, which resulted in the phase transformation from the layered $(R\bar{3}m)$ to the spinel $(Fd\bar{3}m)$ and/or rock-salt $(Fm\bar{3}m)$ phase.^{79,105,106} The phase transformation process produces strains that can promote the formation of cracks. Other examples, such as LCO, also prove that phase transformation at a high cut-off voltage accounts for structural instability and crack formation.57 To conclude, evolution of the crystal structure is one of the primary reasons for crack formation.

Propagation of dislocations. Intragranular cracks have negative impacts such as lattice oxygen release, transition metal and Li mixing, and rock-salt structure formation.⁷⁰ The nucleation and propagation of intragranular cracks are mostly

related to dislocations. Primary particles have random orientations, and they are densely packed. Processes such as electrochemical cycling and high temperature calcination can produce strains between primary particles. The induced strains cannot be consistently accommodated which leads to the generation of dislocations. The propagation of dislocations^{38,64,96,107} can lead to the formation of two categories of intragranular cracks: premature intragranular cracks (pink arrows in Fig. 12(a)) and mature intragranular cracks (yellow arrows in Fig. 12(a)).³⁸ It is believed that the mature intragranular cracks are developed from the premature ones. The HAADF-STEM image in Fig. 12(b) shows that the width of the premature cracks was about 0.72 nm, which was caused by the splitting of two neighboring transition metal slabs and propagation along the (003) planes. This observation explains how the intergranular cracks were predominantly parallel to the (003) planes in the layered structure. Furthermore, the annular bright-field (ABF) STEM image in Fig. 12(c) shows that the interslab between two transition metal layers was not empty, which proves that the premature cracks were formed by the loss of transition metal layers. The inset circles in Fig. 12(d) are the TEM images of the cathode particles cycled at different cut-off



Fig. 12 (a) Observation of the intragranular cracks along the (001) plane in the NMC333 cathode from HAADF images. The yellow arrows indicate mature cracks and the pink arrows indicate premature cracks. The scale bar is 50nm. The STEM images of the same premature cracks under (b) HAADF and (c) ABF mode. (d) The HAADF-STEM images showing that intragranular crack formation in NMC333 is governed by the cut-off voltage. (e) Schematic illustration of the dislocation-assisted crack incubation, propagation and multiplication processes.³⁸ Used with permission from ref. 38.

voltages. From Fig. 12(d), the authors pointed out that the propagation of dislocations is an electrochemically activated process, because intragranular crack formation directly correlates with high voltage cycling. However, this argument might not be strong enough, since more Li ions can be extracted from the cathode material under high cut-off voltage conditions, inducing more volume change and microstrain, which might also be responsible for the intragranular crack formation. Fig. 12(e)shows an overall scheme showing the intragranular crack evolution process: electrochemical and thermal processes initiated the occurrence of dislocations, which then propagated along the transition metal layer direction and formed intragranular cracks. Nevertheless, the actual formation mechanism is still not well understood, and there are very few reports on this topic. Thus, more investigation is required for a better understanding

Lattice oxygen release. Lattice oxygen release from the cathode material^{35,70,108} also contributes to intragranular and intergranular crack formation since it is related to phase transformation (from the layered structure to the spinel and/or rock-salt structure)79 and strain accumulation.109 Lattice oxygen release can be induced by overcharging of the cathode material110,111 or thermal abuse conditions.35 Moreover, lattice oxygen release is not homogeneous^{35,112} (Fig. 13(a)) at the secondary particle level due to the different orientation-dependent oxygen release rates.¹⁰⁶ We observed an inhomogeneous Ni valence state distribution at the secondary particle level, which is an indication that the oxygen release is also heterogeneous, since oxygen release is associated with the reduction of Ni due to the Ni3d-O2p hybridization.113,114 The oxygen release-induced strain, such as mismatch strain and shear stress, cannot be accommodated by the randomly orientated primary particles and it can be released through the formation of cracks along the weakest regions- grain boundaries (Fig. 13(b)). Grain boundaries are the weakest regions since primary particles are randomly orientated and the volume change is anisotropic. The intergranular crack formation can ultimately lead to the detachment of primary particles, as mentioned earlier in this paper. Furthermore, the oxygen vacancy evolution showed that the surface is subjected to more oxygen loss and subsequently more volume change (Fig. 13(c)). The induced tensile stress between the bulk and the surface further adds up to the grain boundary strain and initiate a radical intragranular crack from the bulk (Fig. 13(d)), in addition to the observed intergranular crack.

Three main crack formation mechanisms are reviewed in this section. First, evolution of the crystal structure produces strain in the cathode material because of the volume expansion/ contraction. The accumulated strain is released through the formation of cracks. Second, the initiation of defects (*e.g.*, dislocations) is inevitable and associated with the material synthesis process. The propagation of dislocations induces the formation of intragranular cracks. The growth of intragranular cracks can potentially lead to the formation of intergranular cracks. Third, oxygen release, which leads to the phase transformation and strain accumulation, can also promote the chemomechanical breakdown of LCMs. Here we emphasize that these crack formation mechanisms are not independent of each other, for example, evolution of the crystal structure can produce strain that promotes the initiation of dislocations.

4. Ways to enhance the chemomechanical properties

Chemomechanical breakdown of LCMs is thought to be one of the key reasons that lead to capacity fading of LIBs and it has been intensively observed. To date, there has been a limited number of reports that investigate how the chemomechanical properties of LCMs can be enhanced or the negative effects of cracking can be reduced. We summarized current methods that can either mitigate the crack formation or reduce the negative impacts of cracks.

Surface engineering

Surface engineering¹¹⁵ can mitigate undesired cathode-electrolyte side reactions and reduce surface crack formation. Two main mechanisms are proposed for the function of the coating layer. The first mechanism behind coating is that the coating layer can work as a barrier to the electrolyte infiltration effect. A solid electrolyte Li₃PO₄ (LPO) coating to NMC primary particles68,116 was achieved by atomic layer deposition (ALD)117 and low temperature annealing (Fig. 14(a)).116This solid electrolyte layer could prevent the electrolyte infiltration; thus the extent of cathode-electrolyte reactions was reduced. The second mechanism behind coating is that the coating layer works as an HF scavenger. HF is a strong acid, and it can react with LCMs which can lead to transition metal dissolution and electrolyte decomposition. By consuming the hazardous HF, the undesired reaction between the electrolyte and active cathode material can thus be mitigated.¹¹⁸⁻¹²⁰ Methods that adopt the second mechanism include depositing a MgAl₂O₄ coating on LCO,¹²¹ Al₂O₃ coating on NMC,¹²²⁻¹²⁴ and Co₃(PO₄)₂ coating on NCA.¹²⁵ The Al₂O₃ coating layer is chemically inactive to the electrolyte and it works as a protection layer for the NMC material under high cut-off voltage (>4.4 V) conditions, since it mitigates the side reaction between the electrolyte and the highly active Ni sites.

A novel method, gradient structure design, can also be categorized as a surface engineering method. A Mn-rich NMC material is highly stable with low discharge capacity since Mn is electrochemically inactive. A Ni-rich NMC material, in contrast, is low in stability with high discharge capacity. A core-shell structure design of the cathode material was achieved with Mnrich NMC as the shell and Ni-rich NMC as the core at the secondary particle level (Fig. 14(b)).126 This design significantly improved the stability of NMC materials. The core-shell structure was further developed to a full concentration gradient structure,127,128 in which the Ni-content decreased linearly and the Mn content increased linearly from the core to the surface (Fig. 14(c)). With the full concentration gradient structure, the initial capacity of LiNi_{0.75}Co_{0.10}Mn_{0.15}O₂ could reach \sim 215 mAhg⁻¹ with a capacity retention of more than 90% after 1000 cycles at 1C. The primary reason for this excellent



Fig. 13 (a) Finite element modeling (FEM) model of multiple randomly orientated NMC grains. (b) Phase transformation-induced evolution of shear stress and formation of intergranular cracks along the grain boundaries. (c) Surface and bulk oxygen vacancy distribution. (d) Oxygen release-induced nucleation and propagation of intragranular cracks in NMC.³⁵ Used with permission from ref. 35.

performance is that the near surface region was stabilized with the Mn-rich NMC material.

Grain engineering

In a secondary cathode particle, most primary particles are randomly orientated. During the electrochemical cycling process, anisotropic volume change-induced microstrain cannot be concordantly accommodated, which initiates the formation of cracks. Sun and co-workers successfully enhanced the chemomechanical properties of cathode particles by grain engineering.^{56,129} The grain engineering method is based on a two-sloped full concentration gradient (TSFCG) design and rod-shaped primary particles. Cathode particles with the TSFCG design have two gradient slopes: from the core to the nearsurface region, the concentration gradients for each transition metal are smooth, whereas from the near-surface region to the surface, the concentration gradients for transition metals change abruptly. The TSFCG design can be achieved with a coprecipitation method by tuning the ratio of transition metals in the reagent.^{130,131} In addition to the TSFCG design, another important feature of this advanced design is columnar grains, which are formed by the rod-shaped primary particles.¹²⁹ Without grain engineering, primary particles have random orientations, which makes the secondary particle mechanically unstable (Fig. 15(a–c)). Grain engineering significantly enhances the chemomechanical properties of the cathode material (Fig. 15(d–f)). The underlying reason for the enhanced chemomechanical properties is that the highly correlated particle orientation can reduce the anisotropic internal microstrain (Fig. 15(g)).

Elemental substitution

Elemental substitution, which is normally known as doping, has been intensively investigated, and is an effective strategy to



Fig. 14 (a) Synthetic procedure of LPO-coated NMC. The NMC particle is coated with LPO by ALD, followed by the annealing process.⁵⁵ (b) Schematic diagram of the NMC particle with a Ni-rich core and Mn-rich shell structure.¹²⁶ (c) Schematic diagram of the NMC particle with a full concentration gradient structure. The Ni-content decreases linearly while the Mn content increases linearly from the bulk to the surface.¹²⁷ Used with permission from ref. 55, 126 and 127.

mitigate chemomechanical breakdown. The underlying reasons for improved chemomechanical properties can be attributed to less phase transformation and/or higher structural stability. La and Al co-doping of LCO was proposed recently to reduce phase transformation.57 The chemomechanical properties of LCO were improved by mitigating the order-disorder transition at low voltage and the H1-3 phase transformation at high voltage. The rearrangement of Li vacancies was blocked by the Al³⁺, which served as a fixed charge center due to its smaller size and higher charge over Co²⁺. Readers can refer to more reports on suppressing phase transformation by elemental substitution: Na substitution at the Li site in NMC,¹³² Al substitution at the Mn site in a Li and Mn rich material,¹³³ K doping of a Li rich material¹³⁴ and Zr doping of NMC622 (ref. 135) and LNO.¹³⁶ Elemental substitution can also enhance the chemomechanical properties of the cathode material by enhancing its structural stability. In situ synchrotron XRD measurements showed that Mg substitution in NCA could mitigate the drastic c axis

shrinkage, thus reducing crack formation at high voltage.¹³⁷ The overall volume change after doping was considerably reduced after elemental substitution. Some more reports cover Al doping of NMC¹³⁸ and Mo⁶⁺ doping of NMC333.¹³⁹

Pre-cycling treatment, reduced particle size, and use of electrolyte additives

Pre-cycling treatment means increasing the cut-off voltage from low to high, and an example is increasing the cut-off voltage from 4.5 V by 0.1 V every two cycles to 4.8 V. The pre-cycling method was shown to be effective in mitigating the formation of microcracks at the particle surface.^{58,59} With pre-cycling treatment, the discharge capacity of Li[Ni_{0.17}Li_{0.2}Co_{0.07}Mn_{0.56}]O₂ after 50 cycles reached 250 mAhg⁻¹, while the untreated one only delivered about 200 mAhg⁻¹. However, the physicochemical meaning of this pre-cycling method has not been understood yet.



Fig. 15 (a–f) High-magnification cross-sectional SEM images of $LiNi_{0.82}Co_{0.14}Al_{0.04}O_2$ (NCA82) and TSFCG- $LiNi_{0.85}Mn_{0.10}Co_{0.05}O_2$ (TSFCG85) cathode particles. All of the cathode particles were charged to 4.3 V first and then soaked in the electrolyte for different lengths of time. Cross-sectional SEM images of the NCA82 cathode particles soaked in the electrolyte for (a) 0 day, (b) 1 day, and (c) 3 days. Dramatic crack formation was observed in the NCA82 particle. Cross-sectional SEM images of the TSFCG85 cathode particles soaked in the electrolyte for (d) 0 day, (e) 1 day, and (f) 3 days. No obvious crack formation was observed in TSFCG85 cathode particles. (g) Schematic representation of the NCA82 and TSFCG85 cathode particles. After grain engineering, the uniformly orientated rod-shaped primary particles in TSFCG85 can enhance the chemomechanical properties.¹²⁹ Used with permission from ref. 129.

Moreover, one can also tune the particle size of primary and/ or secondary particles to enhance their chemomechanical properties. Chiang *et al.*⁶⁰ proposed that when the primary particle is below some specific size, the formation of cracks would be dramatically reduced. From our recent study,⁴⁹ we know that small secondary particles are more robust. However, this comes at the cost of inferior tap density and larger surface area. Based on this information, it is recommended to reduce the primary particle size, and at the same time, find a balance between the secondary particle size and better electrochemical performance.

Use of electrolyte additives is another method to enhance the chemomechanical stability of the cathode material. Some electrolyte additives can form a protective layer on the cathode, which can mitigate the undesired side reactions such as transition metal dissolution.^{140,141} This underlying mechanism is similar to that of surface engineering. Moreover, electrolyte additives that work as an artificial HF scavenger can be added⁶¹

to prevent the HF attack on the cathode material. By limiting the presence of HF, chemomechanical breakdown of the cathode can thus be limited. Furthermore, electrolyte additives may help eliminate the surface oxygen loss to effectively limit the intragranular cracks reported in our previous study.³⁵

Each of the aforementioned methods has its own advantages and disadvantages. Surface engineering is a good way to mitigate the side reactions between the cathode and liquid electrolyte, and thus secondary particles are intact after long cycling. However, some surface engineering methods - such as ALD - can be expensive and have high requirements for precursors, which make them less appealing for industrial scale material synthesis. We are aware of increasing efforts to improve the manufacturability of the ALD technique for batteries. Furthermore, some coating layers have low electronic conductivity, which can potentially reduce the cyclability of the cathode. Mechanistically, the exact functions of coating layers are still debatable. It is still unclear how the ion transport takes place across the layers. More studies are needed to address this fundamental question. The gradient structure design, a novel surface engineering method, in contrast, is relatively cheap, easy to accomplish on a large scale, and more importantly, provides good electronic conductivity. Nevertheless, the gradient structure design also has its own drawback: the Mnrich surface induces more Mn dissolution during the cycling process, which can be detrimental to the overall cell performance including the integrity of the SEI on the anode surface. Grain engineering can effectively enhance the chemomechanical properties of cathode materials, but the synthesis of rod-like primary particles can potentially lead to higher cost. Elemental substitution is easy to achieve and is widely used in battery materials chemistry. Certain elemental substitutions may improve the electronic properties of layered oxides. For example, they may improve the oxygen stability142,143 and inhibit the oxygen release-induced chemomechanical breakdown. In summary, we believe that combining the aforementioned methods may lead to dramatically enhanced chemomechanical properties.

5. Chemomechanical breakdown of Na-cathode materials

Na, being in the same alkali group as Li, has similar electrochemistry to Li, and SIBs are one of the most promising energy storage devices for the future, based on the abundant Na resources and low cost.^{144,145} Many Na cathodes have been proposed in a very short time, and some examples are O3 type NaMnO₂,¹⁴⁶ NaTiO₂,¹⁴⁷ and Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O₂,¹⁴⁸P2 type Na_{0.5}[Ni_{0.23}Fe_{0.13}Mn_{0.63}]O₂,¹⁴⁹ Na_{0.6}Co_{0.25}Fe_{0.25}Mn_{0.5}O₂,¹⁵⁰ and Na_{2/3}Ni_{1/3}Mn_{2/3}O₂.¹⁵¹ Here we point out that the explanation of the notation system of the layered structure, such as O3 and P2 can be understood through Delmas's investigation.¹⁵²

Chemomechanical breakdown of Na-cathode materials has also been reported, and a similar formation mechanism to that in LIBs has been proposed: cathode–electrolyte side reactions and evolution of crystal structures. NaPF₆, similar to its counterpart LiPF₆ in LIBs, leads to the inevitable formation of HF, which can give rise to undesired side reactions between the Na cathode and electrolyte. These side reactions will lead to the chemomechanical breakdown of the Na cathode, such as cracking and exfoliation.62 Along with the investigations of chemomechanical breakdown, the concomitant investigations on cathode material stabilization against crack formation are also very significant. Some of such stabilization techniques, including surface engineering, such as formation of Al₂O₃ coatings,^{151,153} and Al₂O₃/multi-walled carbon nanotube hybrid networks,¹⁵³ were proved to be an effective way to reduce those unwanted side reactions. The Na cathode also experiences a volume change due to the intercalation and de-intercalation of Na ions.63 This volume change can produce strains that are hard to accommodate and can be released by the formation of cracks. Some novel Na cathodes, such as Na3TiP3O9N154 and Na2FeSiO4 (ref. 155), were proposed since they have a relatively small volume change and negligible strain. Even though researchers in the Na cathode area are still exploring new materials and ways to enhance the discharge capacity and stability, topics like chemomechanical breakdown of Na-cathode materials need further investigation.

6. Analytical techniques to study chemomechanical properties

Chemomechanical breakdown of battery particles produces three-dimensional defects that undergo complicated chemical and structural transformations at multiple length scales. These defects are delicate enough that they can be destroyed by the experimental operation. Therefore, the characterization of these defects requires a range of nondestructive and 3D sensitive analytical techniques. X-ray and electron microscopic techniques are suitable for visualizing cracks, which have been done extensively in the field.^{156,157} Only very recently, the field has moved from the descriptive microscopic analysis to the quantitative determination of cracks.49 As elaborated above, the outcome of crack formation can induce chemical and structural transformations that start from the crack surface and propagate into the subsurface. These processes are similar to the surface degradation in most cathode materials. The characterization of these processes is similar to any surface chemistry analysis in battery materials. Over the last few years, we have witnessed many new and improved techniques that are suitable for analyzing chemomechanical breakdown. This review by no means covers all of these techniques; thus we selectively discuss the ones that are emerging and relatively unexplored by the broad battery community. Readers are recommended to refer to some of the recently published comprehensive review articles regarding advanced characterization of battery materials.158-164

Electron microscopy (EM) represents one of the most popular techniques that are widely available in a standard academic laboratory. Many of the aforementioned studies relied solely on EM. In general, EM can provide quick assessments of chemomechanical properties by directly visualizing the cracks. TEM and SEM are complementary to each other in terms of spatial resolution. The powerful structural analysis capability of electron diffraction and EELS can reveal the most relevant information about the local chemistry. However, battery materials, in particular LCMs, are usually electron beam sensitive.¹⁶⁵ Special attention is recommended when analyzing the delicate local chemistry in the vicinity of cracks. Fractured particles can be observed with TEM^{5,11} and FIB-SEM.⁴¹

Synchrotron X-ray based imaging techniques have experienced a rapid development over the last few years. The associated imaging processing and data analysis, especially with the big data and machine learning approach, are capable of pinpointing some finer details that were difficult to obtain in the past. Spectroscopy-based X-ray imaging, coupled with 3D reconstruction, allows for almost nondestructively visualizing the 3D chemical and morphological information.¹⁶⁶ With a single voxel of 30 nm \times 30 nm \times 30 nm, there are numerous spectra in a single battery particle; thus the data analysis can become enormous without a high-throughput analysis method. To overcome such a challenge, Liu and coworkers¹⁶⁷ have developed a machine learning methodology to identify functionally important minority phases (*e.g.*, metallic Co) in LCO

battery particles after cycling. They achieved this with a data set of over 10 million spectra collected from more than one hundred particles. This approach and the associated novel clustering algorithms open the door for analyzing the local chemistry with a spatial resolution in the vicinity of cracks. They also enable the path towards decoupling local chemistry from the global chemistry. TXM, with a similar spatial resolution to SEM, can probe the distribution of microcracks inside battery particles.

Recently, we studied the dependence of crack formation on the charging rate (Fig. 13). After 50 cycles at different rates, active particles were collected from the electrodes and analyzed by TXM. We observed that the crack density increased with the increase of charging rate (Fig. 16(a)). We then mathematically processed the tomography data and quantified the porosity and surface area of these particles, which increased as the crack density increased (Fig. 16(b)). To the best of our knowledge, this is the first time that the chemomechanical breakdown was quantified three dimensionally. We believe that such a quantification is important to understand the impact of crack formation on the cathode–electrolyte interfacial chemistry. The



Fig. 16 Qualitative and quantitative characterization of cracks in NMC particles: (a) reconstructed 3D and 2D particles from TXM data. The particles are in the as-prepared state and after 50 full cycles at 1C, 2C, 5C and 10C. The 2D slices are through the centers of the particles. Evolution of (b) the porosity and the specific crack surface area, and (c) the crack induced diffusion deterrent and the unaffected regions as a function of cycling rate.⁴⁹ Used with permission from ref. 49.

increased surface area can potentially improve the infiltration of the electrolyte solution in the active particles, but it also inevitably increases the likelihood of cathode–electrolyte interfacial side reactions, such as surface reconstruction, electrolyte oxidation, and metal dissolution. Furthermore, the formation of microcracks in individual active particles can interrupt the continuity of electron transport, as electrons can only travel through the solid but not through the microcracks (Fig. 16(c)). As the charging rate increased, the travel distance for electrons from inside the particle to the surface got longer.

In the earlier part of this review, we have discussed TXM for mapping the charge distribution in battery secondary particles, and the method can be well integrated with the analysis of cracks. There is a complex interplay between internal stress and the charge distribution. The heterogeneous distribution of internal stress can lead to a non-uniform charge distribution. On the other hand, the non-uniform charge distribution causes spatially dependent structural changes and thus internal stress. The outcome of this interplay is the formation of microcracks. Further studies can combine the crack quantification with charge distribution mapping to establish the relationship between crack density and charge heterogeneity.

Although synchrotron X-ray spectroscopic imaging offers a powerful tool to study chemomechanical properties, it has a few drawbacks and needs further development. First of all, the speed of data collection handicaps the *in situ* capability. Most Xray spectroscopic imaging techniques need tens of minutes or even hours to complete a meaningful data set for the area of interest. However, chemomechanical processes are usually dynamic and take place on a small time scale. Therefore, *in situ* monitoring of cracks, especially their inception, is probably the next frontier. Second, the spatial resolution limits us to only observing intergranular cracks for polycrystalline materials.

At the atomic scale, the formation and propagation of microcracks are mediated by line defects such as dislocations. Some progress has been made in mapping dislocations inside battery particles (Fig. 17(a-c)).⁶⁴ Bragg coherent diffraction imaging is a powerful tool in characterizing the edge dislocation displacement field. The evolution of dislocation lines at different charge states can then be built based on the



Fig. 17 (a–c) Topological defect evolution in a cathode particle under operando conditions. (a) Displacement field for a cross section of a cathode particle. (b) Direct view of the edge dislocation line evolution at different charging states. (c) Direct view of the same edge dislocation line evolution (b) from a different direction.⁶⁴ (d) Evolution of the strain distribution inside a cathode particle under different charging conditions. Blue and red represent the α and β phases, respectively, for the cross sections at 8.143 and 8.142 Å.⁶⁵ Used with permission from ref. 64 and 65.

displacement field.⁶⁴ Understanding the topological defect dynamics provides valuable information for future defect manipulation. In addition, studying the spatial distribution of strain dynamics in battery particles has been made possible (Fig. 17(d)).⁶⁵ With knowledge on strain dynamics, we can further find the correlation between strain evolution and other factors, such as charge depth and chemical composition. The information from strain dynamics is also instructive for future materials design.

Moreover, many other state-of-the-art characterization methods are applied to study the structural evolution and mechanical properties. Neutron diffraction¹⁶⁸ has been applied to study the evolution of the crystal structure. Nano-indentation¹⁶⁹⁻¹⁷¹ has been used to measure the elastic, plastic, and fracture properties of cathode materials. All these aforementioned characterization methods provide significant insights into our future work.

7. Conclusions and perspectives

Alkali metal ion batteries have drawn much attention due to their current and future application in energy storage systems of different scales. However, chemomechanical breakdown of LCMs, which is partially responsible for the capacity fading in alkali metal ion batteries, remains unsolved. This review summarizes recent progress in characterizing, understanding, and modifying the chemomechanical behaviors of LCMs in alkali metal ion batteries. Details of the negative effects, impacting factors, formation mechanisms, modification methods, and characterization techniques of chemomechanical breakdown have been discussed in this review. Intragranular and intergranular cracks in LCMs can lead to poor electronic conductivity, loss of active material, more severe cathode-electrolyte side reactions, and a higher extent of transition metal dissolution and SEI formation interruption. Intrinsic factors (Ni-content, and primary and secondary particle size) and extrinsic factors (charge depth, charging and discharging rate, and cycle number) can affect the formation of cracks. Formation mechanisms of cracks, such as the evolution of the crystal structure, propagation of dislocations, and oxygen release, are addressed in detail. In addition, surface engineering, elemental substitution, pre-cycling treatment, reducing particle size, and use of electrolyte additives are good ways to mitigate the formation of cracks. Cracks in SIBs are also briefly covered in this review. Finally, light is shed on the new analytical techniques that have been applied to the study of cracks.

The successful commercialization of LIBs has profoundly improved the quality of our lives in the past three decades. To make our society a sustainable one, large energy storage systems have imposed much stricter performance requisites on LIBs and SIBs. Therefore, chemomechanical breakdown of cathode materials, one of the main capacity fading mechanisms, must be restrained for higher performance LIBs and SIBs. Chemomechanical breakdown of layered oxides has been intensively observed, yet its formation mechanism remains vague.

LCMs provide a good platform for the fundamental crystallographic research because of the diverse phase transformations during electrochemical cycling. LCMs, except LCO, are formed by randomly orientated single crystals. During the charging/discharging process, LCMs experience nucleation and propagation of defects (e.g., dislocations). A better understanding of the properties of LCMs not only provides scientific insights into crack formation but also further enriches our knowledge on crystallography. Moreover, the interplay between charge heterogeneity, compositional heterogeneity, and crack formation needs more studies. Understanding the formation mechanisms will give us valuable information regarding nextgeneration advanced design principles. Based on current knowledge, reducing the primary particle size, surface engineering, and advanced nanostructure design are possible solutions. State-of-the-art techniques, such as TXM in combination with machine learning methodology, need further improvement in their spatial and temporal resolution to quantitatively study crack formation under practical operating conditions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge support from the National Science Foundation under Grant no. DMR-1832613. The work was also supported by the Department of Chemistry Startup at Virginia Tech. Use of the SSRL, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. The authors acknowledge Yao Wang (Rice University, TX, USA) for her help in making figures.

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