

Heterogeneous Reaction Activities and Statistical Characteristics of Particle Cracking in Battery Electrodes

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Supporting Information

The chemomechanical breakdown of electrodes can interrupt the stable operation of batteries.^{1–4} Particle cracking can take place in nearly all electrode materials.^{3,5} In addition to the microstructural evolution of the active electrode, particle cracking can cause complex reactions with the electrolyte and instigate a rapid performance degradation.^{6,7} Chemomechanical properties have also become a focal point of research in solid-state batteries.⁸ Interested readers may refer to refs 3 and 9 to get more information about the negative impacts of chemomechanical breakdown. The chemomechanical breakdown is localized and dispersed heterogeneously in composite electrodes. Such complexity of mechanical damage is caused by the redox heterogeneity, which is also dependent on the local chemical environment.^{10–15} For example, in a cathode of Li-ion batteries, crystal defects could cause geometrically non-optimal diffusion pathways at the single grain level (Figure 1a);^{12,16} extended defects (e.g., grain boundaries and cracks)¹⁷ result in mesoscale charge heterogeneity in secondary particles that are thermodynamically stable and persist in a long-term operation (Figure 1b);^{18,19} and the spatial arrangement of multiple phases in the composite electrode (active particles, inactive conductive additives, and micropores) further induces different degrees of electrochemical activities and particle utilization (Figure 1c).²⁰

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and biased information? The rapid development of analytical techniques has opened the door for precisely probing the dynamic process of mechanical degradation at different length scales. Here we elaborate the raised question in the context of a few state-of-the-art material characterization tools and their advantages and disadvantages, including electron microscopy and X-ray imaging techniques (Supporting Information).

The heterogeneous nature of electrochemical reactions and mechanical degradation places a daunting challenge in electron and X-ray characterizations.^{21–24} Recent large-scale electrode studies have uncovered that particle cracking is highly heterogeneous in composite electrodes. There are fundamental reasons and practical implications of such heterogeneity, which is ubiquitous even in the best-optimized commercial battery electrodes.^{17,25–27} Figure 2 exemplifies such heterogeneity in a section of a practical electrode containing thousands of active particles. In a well-prepared academic electrode (Figure 2a), the degree of damage heterogeneity is overwhelmingly significant. Without a thorough investigation with specific attention paid to the statistics, we found that different biased conclusions could be made, as discussed below.

When we select only one particle to represent the damage level of this electrode, we found that one may draw conclusions all the way from no damage to severe damage. When we chose clusters of a few particles to present, we still observed a significant degree of variation between different clusters (Figure 2a). Although distinct degrees of damage are observed in these two selected clusters, they are only about 100 μm apart in the electrode, highlighting a severely heterogeneous local chemistry. In secondary particles such as polycrystalline layered oxides, the internal crack patterns could be dramatically different from those observed on the external surface. The internal cracks can still be accessible to the electrolytic solution through open microcracks, thus contributing to the electrode–electrolyte reactions.⁶ Such reactions can be either beneficial or detrimental to the battery performance.

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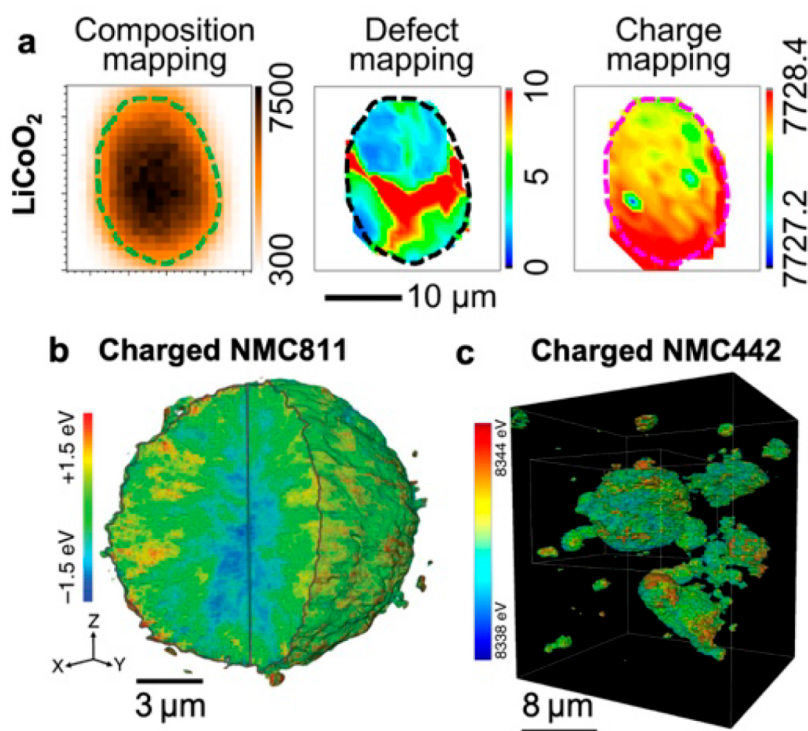


Figure 1. Heterogeneous reactions in the cathode of Li-ion batteries. (a) A LiCoO_2 single grain, where edge dislocations impact the charging reactions. The color code in the defect mapping represents the concentration of edge dislocations. The color code in the charge mapping represents the Co K-edge energy. Adapted with permission from ref 12. Copyright 2020 John Wiley & Sons, Inc. (b) Charged $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) secondary particle, where a highly heterogeneous shell-to-core charge propagation is observed. The color bar represents the relative Ni K-edge energy, where a higher value represents a higher state of charge. Reprinted from ref 19. Published open access, licensed under a Creative Commons Attribution 4.0 International License, by Springer-Nature 2020. (c) Charged $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ (NMC442) secondary particle ensembles. The color bar represents the Ni K-edge energy, where a higher value represents a higher state of charge. Reprinted from ref 20. Published open access, licensed under a Creative Commons Attribution 4.0 International License, by Springer-Nature 2018.

On one hand, cracks open up fresh surfaces to provide more ion intercalation sites, temporarily promoting reaction kinetics. On the other hand, these new surfaces may undergo surface reconstruction²⁸ to form densified interphase layers that impede the Li-ion diffusion in the long run. Therefore, the buried internal cracks play a significant role in affecting the battery performance. Moreover, these secondary particles could exhibit mesoscale pores, which could benefit reaction kinetics but are detrimental to the effective packing density. Without the capability of detecting the buried cracks and pores, the topographic imaging methods, e.g., top-view scanning electron microscopy (SEM), might miss some of the key information. Here we provide examples of particles with similar surface profiles but strikingly different internal cracking patterns (Figure 2b, with the surface renderings on the left and the corresponding virtual slices on the right). Next, we consider the reliability of the lab-based, focused ion beam (FIB)-prepared cross-section samples. FIB cross-sections have been widely applied to examine the internal structure of battery electrodes and solid electrolytes. Here we present the cross-sections of the NMC electrode (Figure 2c) with selected particles of very different damage degrees enlarged in Figure 2d. Since we construct the cross-section from large-scale phase contrast X-ray tomography, we can show the cross-sections spanning a more extensive area compared to the standard SEM cross-sections reported in most studies.^{29,30} We observe a significant degree of variation between different cross-sections

of the same electrode. To increase statistical representativeness, we recommend that FIB cross-section be performed for a large area and over different depths.

In general, electrode preparation can greatly influence the chemomechanical response of battery particles during electrochemical cycling. Most commercial electrodes would undergo calendaring³¹ before the cell manufacturing, which could cause residual stress on the particles and influence the subsequent chemomechanical characterization. Electrochemical cycling conditions, such as charging/discharging rate, temperature, voltage windows, and electrolytes, all critically affect the particle cracking behavior.^{3,5,32} We acknowledge that numerous other factors can influence the degree of heterogeneous chemomechanical breakdown. For example, whether a particle is hollow or solid at its pristine state³³ and how its primary crystal grains are spatially oriented³⁴ could both modulate the way that the mechanical strain is distributed, relaxed, and accumulated over time. The purpose of this Viewpoint is not to argue whether the heterogeneous damage of battery particles is caused by the experimental conditions. Instead, we would like to stress that, within the same electrode, different conclusions may be drawn based on different experimental protocols in the sample characterization if the statistical significance is not properly addressed. Advanced electrode manufacturing techniques, e.g., magnetic field directed assembly³⁵ and 3D printing,³⁶ could potentially produce well-structured electrodes with ordered particle

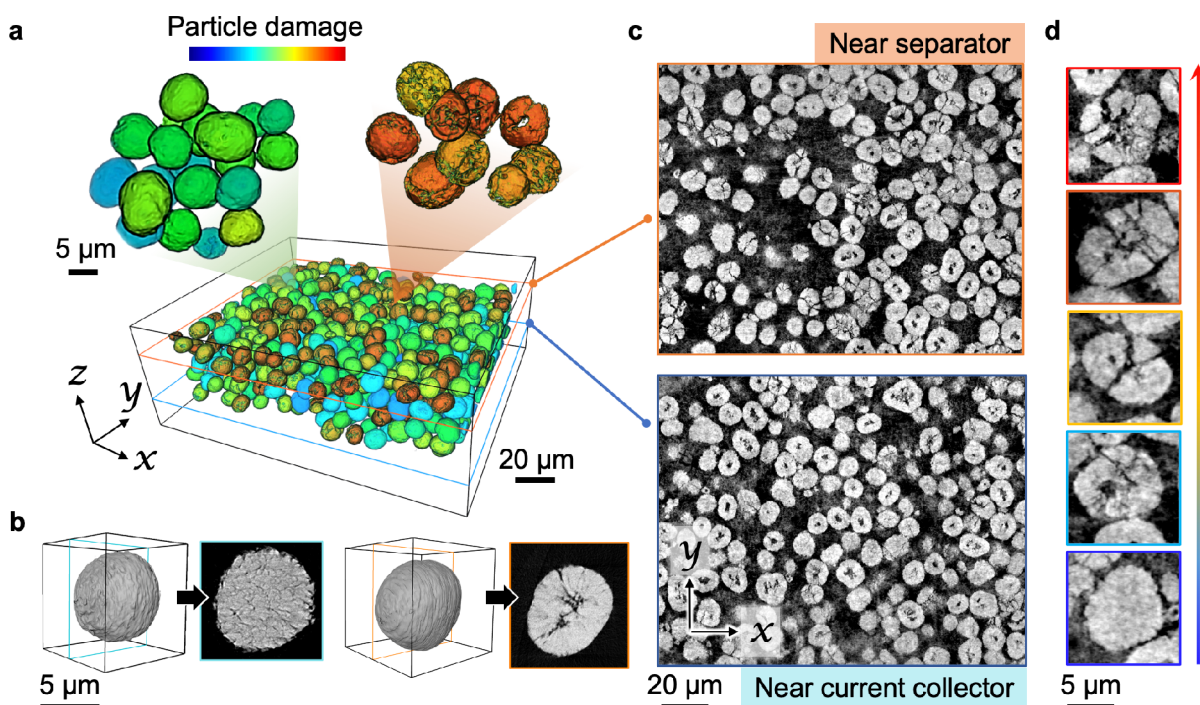


Figure 2. Heterogeneous particle damage in a well-formed NMC composite cathode. The particles in panel (a) are color-coded to their respective damage degrees. Two clusters with significant differences are enlarged for better visualization. Panel (b) shows two particles that demonstrate similar shapes when viewed from the exterior but exhibit very different internal structures, as revealed by their respective virtual 2D slices. Two distinct virtual slices at different depths over the same electrode are shown in panel (c). Panel (d) shows a few selected particles within the imaged electrode, demonstrating various degrees of particle cracking.

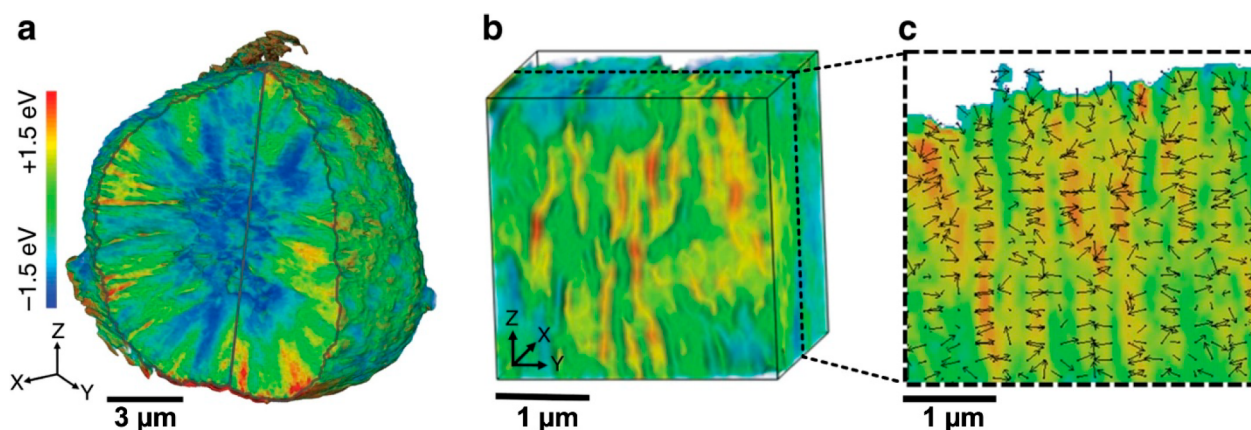


Figure 3. Surface and bulk redox heterogeneity in NMC particles. Panels (a) is a 3D visualization of the Ni redox heterogeneity within an NMC particle with radially aligned primary grains. Panels (b) and (c) are the 3D and 2D views of a sub-particle region from panel (a). Reprinted from ref 19. Published open access, licensed under a Creative Commons Attribution 4.0 International License, by Springer-Nature 2020.

arrangements. It is, however, still challenging to eliminate the electrode-level charge heterogeneity, which is partially due to the varying electron and ion accessibility at different locations in the electrodes. Reducing the electrode thickness can potentially suppress or eliminate the concentration gradient in the thickness direction. However, the lateral heterogeneity could persist even in the well-ordered thin electrode due to varying stack pressure. Furthermore, a recent study suggested that the intrinsic thermodynamic properties of electrode materials, such as the sensitivity of equilibrium potential to the state-of-charge (SOC), also impact the uniformity of reactions.³⁷

There are unavoidable limitations in some complicated experiments, setting a practical limit on how many particles one could study with a reasonable amount of effort. For example, the *in situ* and *operando* measurements of battery particles' responses to an externally applied reaction driving force (e.g., charging, thermal conditions) are often carried out on a small number of particles.^{38,39} It is also not possible to scan many particles using the 3D X-ray spectro-tomography method, which is a rather time-consuming measurement. In these characterizations for single particles or even local nanodomains, special attention is also warranted for improving the statistical representativeness. Multiple studies have shown that SOC distribution is heterogeneous not only in polycrystal-

line layered oxide particles (Figure 3) but also in single-crystal layered and spinel oxides. Xu et al. reported that the SOC distribution in polycrystalline NMC particles is guided by the crystallographic orientation of the primary grains.¹⁹ The authors also performed a voxel-to-voxel analysis for about 20 million voxels to demonstrate the wide SOC distribution in individual secondary particles (Figure 3). The local SOC heterogeneity influences the chemomechanical stability. Therefore, the characterization techniques with high spatial resolution would need to screen many local nanodomains in the particle to obtain statistical representativeness. In a recent study, Jiang et al.⁴⁰ applied a soft X-ray nanoprobe technique to reveal the highly heterogeneous SOC distribution at the particle surface, consistent with the SOC tomography results reported by Xu et al.¹⁹ (Figure 3a). Such a complex system truly imposes remarkable challenges for characterization studies using techniques at a small length scale.

The materials electrochemistry in batteries is perhaps one of the most challenging systems of complex spatiotemporal heterogeneity. It has remained and will continue to be a challenge to bring together materials characterization at all relevant length scales. There is still a considerable gap between the current state-of-the-art and our ultimate goal of fully understanding the chemomechanical complexity in battery materials. Furthermore, the availability of experimental tools varies greatly across different research groups and countries. Nevertheless, we believe that improving data representativeness is critical and should be carefully addressed by researchers in the field.

In summary, we have noticed that current characterization literature has not considered multiscale heterogeneity enough. Multiscale chemomechanical heterogeneity is one of the underlying reasons for the underuse of the electrode capacity, causing locally overcharged and undercharged regions. If we can eliminate the charge heterogeneity, we can potentially improve the energy density and cycle life of the “old” commercialized battery materials. Through this Viewpoint, we hope to bring attention to the fact that biased conclusions can be made if no systematic, careful characterization is conducted. We recommend some strategies to improve the interpretation of mechanical properties and their relationship with battery performance:

- (1) Perform particle fracture characterization at different cycle numbers and different SOC levels to understand how particle fracturing initiates and propagates.
- (2) Perform *in situ* measurements in a practically relevant sample environment (e.g., pouch cell).
- (3) Integrate the chemomechanical measurements with electroanalytical tools, such as electrochemical impedance spectroscopy.
- (4) Study as many particles and local domains as possible when using high spatial resolution tools.
- (5) *In situ* characterization is not consistently more elite than *ex situ* experiments, so combining *in situ* and *ex situ* measurements at different time and length scales can deliver a more complete picture.
- (6) 3D tomographic reconstruction with bulk microstructure sensitivity can provide more information than topographic imaging.
- (7) Perform experimental and modeling studies as independently as possible, so that no finite tuning of


modeling parameters is performed to artificially improve the consistency.

- (8) Combine mechanical characterization with chemical analysis to understand the interplay between mechanics and chemistry.

Materials characterization has undergone a rapid development period in the past decade because of the need for better tools in battery research. With electron microscopy becoming more statistically representative and synchrotron X-ray techniques achieving higher spatial resolution while maintaining a large field of view, we believe that more will be uncovered regarding chemomechanical heterogeneity. Furthermore, the implementation of data analysis methods such as machine-learning approaches will shed light on a comprehensive understanding of the complex behavior of batteries. Riding on the learning curve, we call for an effort to tackle the frontier challenges in battery science with advanced and statistically significant materials characterization techniques. While our Viewpoint focuses on Li-ion cathodes, the opinions expressed here can be applied to investigate many more electrode materials, such as anodes with large volume changes.

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■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenergylett.1c02135>.

Discussion of electron microscopy and X-ray imaging techniques and their advantages and disadvantages (PDF)

■ AUTHOR INFORMATION

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsenergylett.1c02135>

Notes

The authors declare no competing financial interest. Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

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