# Supporting Information

# Heterogeneous reaction activities and statistical characteristics of particle cracking in battery electrodes

Feng Lin[1*], Kejie Zhao[2*], Yijin Liu[3*]

1. Department of Chemistry, Virginia Tech, Blacksburg, VA 24073, USA. Email: fenglin@vt.edu
2. School of Mechanical Engineering, Purdue University, West Lafayette, IN 47907, USA. Email: kjzhao@purdue.edu
3. Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA. Email: liuyijin@slac.stanford.edu

Electron and X-ray probes are arguably the most popular diagnostic tools for studying mechanical damage under *ex situ* and *in situ* conditions.[1-3] Particle cracking can initiate from both within primary grains (intragranular crack) and along grain boundaries (intergranular crack) in polycrystalline battery particles.[4] A typical example is the polycrystalline $LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC) cathodes.[5, 6] The secondary particles consist of nano-sized primary grains either in random or ordered crystallographic arrangements. Electron probes, such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM), offer high spatial resolution for identifying the initiation and propagation of crystal defects as well as tracking the development of crystal defects into large-scale particle cracks.[7] Because of their wide availability and relative ease of operation, TEM and SEM have become the go-to techniques for battery researchers to investigate the fading mechanism associated with the chemomechanical breakdown. At the atomic scale, the initiation of microcracks is often associated with the formation of oxygen vacancy and vacancy clusters.[8] With the electron tomography method, very fine cracks and voids in nanosized primary grains can be visualized.[9] Thus far, most TEM characterizations have been limited to the microscopic and spectroscopic investigations over a localized region, and it has remained a major challenge to perform many-particle, many-region measurements with statistical significance. Recognizing this challenge, one could take the action to develop experimental methods and data

analytics to improve the throughput and, thus, the statistics of the TEM data for battery material studies. SEM can increase the measuring length scale to secondary particles and electrodes. Thus, SEM, in principle, can be used to investigate particle cracking in a statistically significant fashion by screening many particles in each sample of interest. Furthermore, coupled with the focused ion beam (FIB) technique, FIB-SEM can also offer three-dimensional (3D) imaging capabilities to visualize chemomechanical events.[10] SEM can image low-Z elements with good imaging contrast, making it an ideal tool to investigate carbon and polymer materials. This is a unique advantage over conventional X-ray imaging methods. However, FIB-SEM is a destructive technique, which inhibits *in situ* or *operando* studies using this method.

In comparison, X-ray techniques provide complementary capabilities to overcome some of the challenges facing the electron probes. In particular, the rapid methodology development in synchrotron X-ray imaging techniques have created enormous opportunities for characterizing relatively large-scale chemomechanical events, such as at the secondary particle and electrode levels.[11] Synchrotron X-ray techniques can characterize battery materials and electrodes in a nearly nondestructive manner. Furthermore, due to the strong penetrating capability of hard X-rays (energy > 4 keV), synchrotron X-ray techniques offer an unprecedented platform for investigating battery chemistries under operating conditions for cells ranging from academic coin cells to large-format commercial cells.[12-14] With the phase contrast capability, it has now become possible to differentiate the active and inactive components in a composite electrode with good fidelity.[15] Compared with the electron probes, synchrotron X-ray imaging is more adaptable to monitor the development of particle cracking in a statistically significant manner because of its capability to simultaneously visualize many particles in a geometrically tunable fashion: two dimensions (2D) and three dimensions (3D). Clearly, such an advantage comes with a reduction in the spatial resolution, which needs to be carefully considered depending on the targeted features of interest. The limited availability of synchrotron facilities is another major drawback considering the high demand from the general battery research, which, in turn, has motivated recent follow-up developments of battery electrode characterization using nano-tomography with a laboratory x-ray tube.[16]

## References


(1) Bi, Y.; Tao, J.; Wu, Y.; Li, L.; Xu, Y.; Hu, E.; Wu, B.; Hu, J.; Wang, C.; Zhang, J.-G.; Qi, Y.; Xiao, J., Reversible planar gliding and microcracking in a single-crystalline Ni-rich cathode. *Science* **2020**, *370* (6522), 1313-1317.

(2) Wei, C.; Xia, S.; Huang, H.; Mao, Y.; Pianetta, P.; Liu, Y., Mesoscale Battery Science: The Behavior of Electrode Particles Caught on a Multispectral X-ray Camera. *Acc. Chem. Res.* **2018**, *51* (10), 2484-2492.

(3) Xu, Z.; Hou, D.; Kautz, D. J.; Liu, W.; Xu, R.; Xiao, X.; Lin, F., Charging Reactions Promoted by Geometrically Necessary Dislocations in Battery Materials Revealed by In Situ Single-Particle Synchrotron Measurements. *Adv. Mater.* **2020**, *32* (37), 2003417.

(4) Yan, P.; Zheng, J.; Gu, M.; Xiao, J.; Zhang, J.-G.; Wang, C.-M., Intragranular cracking as a critical barrier for high-voltage usage of layer-structured cathode for lithium-ion batteries. *Nat. Commun.* **2017**, *8*, 14101.

(5) Ohzuku, T.; Makimura, Y., Layered Lithium Insertion Material of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ for Lithium-Ion Batteries. *Chem. Lett.* **2001**, *30* (7), 642-643.

(6) Li, W.; Erickson, E. M.; Manthiram, A., High-nickel layered oxide cathodes for lithium-based automotive batteries. *Nat. Energy* **2020**, *5* (1), 26-34.

(7) Li, Y.; Cheng, X.; Zhang, Y.; Zhao, K., Recent advance in understanding the electro-chemo-mechanical behavior of lithium-ion batteries by electron microscopy. *Mater. Today Nano* **2019**, *7*, 100040.

(8) Mu, L.; Lin, R.; Xu, R.; Han, L.; Xia, S.; Sokaras, D.; Steiner, J. D.; Weng, T.-C.; Nordlund, D.; Doeff, M. M.; Liu, Y.; Zhao, K.; Xin, H. L.; Lin, F., Oxygen Release Induced Chemomechanical Breakdown of Layered Cathode Materials. *Nano Lett.* **2018**, *18* (5), 3241-3249.

(9) Wang, C.; Han, L.; Zhang, R.; Cheng, H.; Mu, L.; Kisslinger, K.; Zou, P.; Ren, Y.; Cao, P.; Lin, F.; Xin, H. L., Resolving atomic-scale phase transformation and oxygen loss mechanism in ultrahigh-nickel layered cathodes for cobalt-free lithium-ion batteries. *Matter* **2021**, *4* (6), 2013-2026.

(10) Liu, Z.; Chen-Wiegart, Y.-c. K.; Wang, J.; Barnett, S. A.; Faber, K. T., Three-Phase 3D Reconstruction of a $LiCoO_2$ Cathode via FIB-SEM Tomography. *Microsc. Microanal.* **2016**, *22* (1), 140-148.

(11) Lin, F.; Liu, Y.; Yu, X.; Cheng, L.; Singer, A.; Shpyrko, O. G.; Xin, H. L.; Tamura, N.; Tian, C.; Weng, T.-C.; Yang, X.-Q.; Meng, Y. S.; Nordlund, D.; Yang, W.; Doeff, M. M., Synchrotron X-ray Analytical Techniques for Studying Materials Electrochemistry in Rechargeable Batteries. *Chem. Rev.* **2017**, *117* (21), 13123-13186.

(12) Qian, G.; Wang, J.; Li, H.; Ma, Z.-F.; Pianetta, P.; Li, L.; Yu, X.; Liu, Y., Structural and chemical evolution in layered oxide cathodes of lithium-ion batteries revealed by synchrotron techniques. *Nat. Sci. Rev.* **2021**, DOI: 10.1093/nsr/nwab146.

(13) Finegan, D. P.; Scheel, M.; Robinson, J. B.; Tjaden, B.; Hunt, I.; Mason, T. J.; Millichamp, J.; Di Michiel, M.; Offer, G. J.; Hinds, G.; Brett, D. J. L.; Shearing, P. R., In-operando high-speed tomography of lithium-ion batteries during thermal runaway. *Nat. Commun.* **2015**, *6* (1), 6924.

(14) Finegan, D. P.; Quinn, A.; Wragg, D. S.; Colclasure, A. M.; Lu, X.; Tan, C.; Heenan, T. M. M.; Jervis, R.; Brett, D. J. L.; Das, S.; Gao, T.; Cogswell, D. A.; Bazant, M. Z.; Di Michiel, M.; Checchia, S.; Shearing, P. R.; Smith, K., Spatial dynamics of lithiation and lithium plating during high-rate operation of graphite electrodes. *Energy Environ. Sci.* **2020**, *13* (8), 2570-2584.

(15) Yang, Y.; Xu, R.; Zhang, K.; Lee, S.-J.; Mu, L.; Liu, P.; Waters, C. K.; Spence, S.; Xu, Z.; Wei, C.; Kautz, D. J.; Yuan, Q.; Dong, Y.; Yu, Y.-S.; Xiao, X.; Lee, H.-K.; Pianetta, P.; Cloetens,

P.; Lee, J.-S.; Zhao, K.; Lin, F.; Liu, Y., Quantification of Heterogeneous Degradation in Li-Ion Batteries. *Adv. Energy Mater.* **2019**, *9* (25), 1900674.

(16) Lu, X.; Bertei, A.; Finegan, D. P.; Tan, C.; Daemi, S. R.; Weaving, J. S.; O'Regan, K. B.; Heenan, T. M. M.; Hinds, G.; Kendrick, E.; Brett, D. J. L.; Shearing, P. R., 3D microstructure design of lithium-ion battery electrodes assisted by X-ray nano-computed tomography and modelling. *Nat. Commun.* **2020**, *11* (1), 2079.