Supplementary information:
Quantifying the impact of charge rate and number of cycles on structural degeneration of Li-ion battery electrodes

Orkun Furat[1,*], Donal P. Finegan[2,*], Zhenzhen Yang[3], Tanvir R. Tanim[4], Kandler Smith[2], Volker Schmidt[1]

[1] *Institute of Stochastics, Ulm University, Helmholtzstraße 18, 89069 Ulm, Germany*
[2] *National Renewable Energy Laboratory, 15013 Denver W Parkway, Golden, CO 80401, USA*
[3] *Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Avenue, Lemont, IL 60439, USA*
[4] *Idaho National Laboratory, 2525 N. Fremont, Idaho Falls, ID 83415, USA*

Supplementary Note S1: Particle porosity across the cathode thickness

In order to investigate whether the crack development depends on the position within the cathode, we determine the local particle porosity as a function of the distance to the separator for pristine cathodes and each degradation scenario (i, j) with $i \in \{1\mathrm{C}, 6\mathrm{C}, 9\mathrm{C}\}, j \in \{25, 225, 600\}$.

For the $m = 9$ SEM images of pristine cathodes we use the functions $\mathrm{surf}^{(i)}_{\mathrm{cathode}}$ and $\mathrm{surf}^{(i)}_{\mathrm{separator}}$ to determine whether a pixel lies between the surface of the cathode and the separator for each $i = 1, \ldots, m$. More precisely, a pixel $x = (x_1, x_2) \in W$ lies between these surfaces of the i-th image if $\mathrm{surf}^{(i)}_{\mathrm{separator}}(x_1) < x_2 < \mathrm{surf}^{(i)}_{\mathrm{cathode}}(x_1)$. On the other hand, a pixel x is associated with the separator or the area outside of the cathode if $x_2 \leq \mathrm{surf}^{(i)}_{\mathrm{separator}}(x_1)$ or $x_2 \geq \mathrm{surf}^{(i)}_{\mathrm{cathode}}(x_1)$ holds, respectively. Therefore, we can extend the phase-wise segmentation $S^{(i)} \colon W \to \{0, 1, 2\}$ (which takes the values 0, 1 or 2 for pixels associated with background, particles or cracks, respectively) with additional labels for the separator and the area outside the cathode (namely, the labels 3 and 4). More precisely, the extended phase-wise segmentation $S^{(i)}_{\mathrm{extend}} \colon W \to \{0, 1, 2, 3, 4\}$ is given by

$$S^{(i)}_{\mathrm{extend}}(x) = \begin{cases} 3, & \text{if } x_2 \leq \mathrm{surf}^{(i)}_{\mathrm{separator}}(x_1), \\ 4, & \text{if } x_2 \geq \mathrm{surf}^{(i)}_{\mathrm{cathode}}(x_1), \\ S^{(i)}(x), & \text{else}, \end{cases} \tag{S1}$$

for each $x = (x_1, x_2) \in W$. Then, we can determine for each pixel $x \in W$ its distance $d^{(i)}_x$ to the separator by

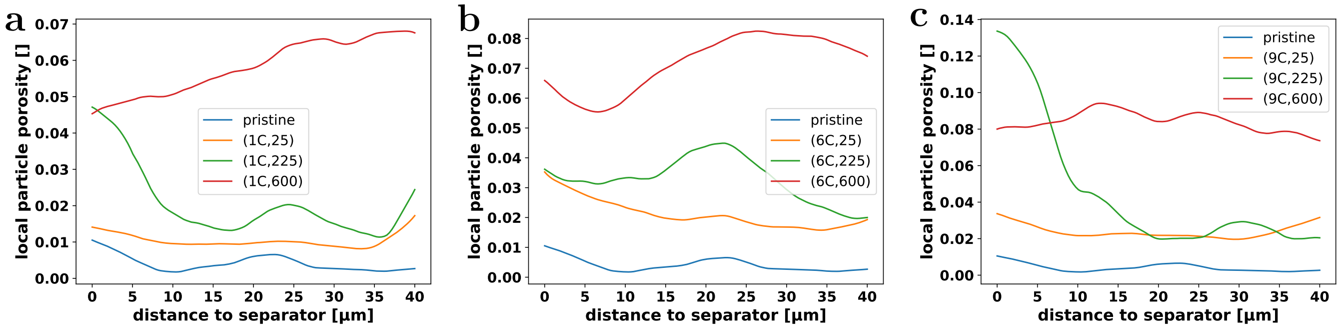
$$d^{(i)}_x = p \min_{y \in W \colon S^{(i)}_{\mathrm{extend}}(x) = 3} \|x - y\|, \tag{S2}$$

where $p = 0.01\,\mu\mathrm{m}$ denotes the pixel size. Note that the local porosity of a pixel $x \in W$ with $S^{(i)}_{\mathrm{extend}}(x) = 2$, i.e., a pixel associated with the crack phase is given by 1. Thus, the set of pairs of distances to the separator and local porosity values of such pixels is given by $\left\{(d^{(i)}_x, 1) \colon x \in W, S^{(i)}_{\mathrm{extend}}(x) = 2\right\}$. On the other hand, the set of such pairs for pixels associated with the particle phase is given by $\left\{(d^{(i)}_x, 0) \colon x \in W, S^{(i)}_{\mathrm{extend}}(x) = 1\right\}$. By considering the union of these sets for each $i = 1, \ldots, m$, we obtain a data set $\mathcal{Z}_{\mathrm{pristine}}$ consisting of pairs of local porosities and the distances to the separator, i.e., $\mathcal{Z}_{\mathrm{pristine}}$ is given by

$$\mathcal{Z}_{\mathrm{pristine}} = \bigcup_{i=1}^{m} \left(\left\{(d^{(i)}_x, 1) \colon x \in W, S^{(i)}_{\mathrm{extend}}(x) = 2\right\} \cup \left\{(d^{(i)}_x, 0) \colon x \in W, S^{(i)}_{\mathrm{extend}}(x) = 1\right\} \right). \tag{S3}$$

By deploying Nadaraya-Watson kernel regression on the dataset $\mathcal{Z}_{\mathrm{pristine}}$ we obtain a regression function for the local porosity in dependence of the distance to the separator, see Figure S1.[34] Analogously, the dataset $\mathcal{Z}_{i,j}$ and the corresponding regression function is determined for each degradation scenario (i, j) with $i \in \{1\mathrm{C}, 6\mathrm{C}, 9\mathrm{C}\}, j \in \{25, 225, 600\}$.

*Corresponding authors
Email addresses: orkun.furat@uni-ulm.de (Orkun Furat), donal.finegan@nrel.gov (Donal P. Finegan)



Supplementary Figure S1: Particle porosity as a function of the distance to the separator for pristine cathodes (blue lines) and the degradation scenarios with a charge rate of 1C (a), 6C (b) and 9C (c).

References

[34] Wand, M. P. and Jones, M. C. *Kernel Smoothing.* Chapman & Hall, London, (1995).