Supporting Information

Characterization of Mechanical Degradation in All-Solid-State Battery Cathode

Tan Shi [a,b†], Ya-Qian Zhang [a,c†], Qingsong Tu [a], Yuhao Wang[a], M.C. Scott[*a,c], Gerbrand Ceder[*a,b]

a. Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA

b. Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

c. The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

†Co-authorship

[*]Corresponding author: Prof. Gerbrand Ceder (Email: gceder@berkeley.edu); Prof. Mary Scott (Email: mary.scott@berkeley.edu)

Experimental Methods

Materials synthesis and characterization: $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC) and $75Li_2S–25P_2S_5$ (LPS) were used as the cathode (CAM) and SE material, respectively. NMC powder ($\overline{D}_{CAM}$ = ~12 μm) was purchased from MSE Supplies LLC. The $Li_2O–ZrO_2$ (LZO) coating (6–8-nm thick) was applied to both NMC powders by Samsung Research Japan using the procedure described by Ito *et al*.[1] The LPS was synthesized by ball-milling stoichiometric amounts of Li_2S (99.98% Sigma-Aldrich) and P_2S_5 (99% Sigma-Aldrich) in a 50-mL ZrO_2 jar for 200 min using a SPEX 8000M mixer mill. The LPS with small particle size used in the composite cathode was prepared by wet ball-milling the LPS SE with heptane and dibutyl ether using a Retsch PM200 ball mill for 40 h. All the LPS synthesis steps were conducted in an Ar atmosphere.

Cell fabrication and testing: Solid-state cells were fabricated in an Ar-filled glovebox (H_2O < 0.1 ppm and O_2 < 0.1 ppm). The composite cathode was made by first hand-mixing 60 mg of the LZO-coated NMC particles and 35 mg of the small-particle LPS for ~10 min. Then, 5 wt% CNFs (from Samsung Research Japan) was added and mixed in for another ~10 min. The cell was assembled using a custom-made pressure cell. A polyether ether ketone (PEEK) cylinder with an inner diameter of 8 mm was used as the insulating body, and two 8-mm-diameter stainless-steel rods were used as current collectors. Next, 35 mg of the LPS electrolyte was added and compressed under ~100-MPa pressure. The cathode composite (~5 mg) was then spread evenly on top and compacted under ~300-MPa pressure. Finally, an 8-mm-diameter piece of In metal was attached as the anode, and ~100-MPa pressure was again applied. The cell was sealed in an Ar-filled jar and cycled under ~2-MPa pressure provided by a spring.

Cell cycling was performed using a Bio-Logic VMP300 system. For all the cells, the cycling voltage window was 2–3.7 V vs. In metal and the current density was 0.05 mA/cm^2. Constant-current constant-voltage (CCCV) charging was used, where the cell was held for 5 h at the top-of-charge state. Electrochmimcal impedance spectroscopy (EIS) was conducted at the end of the discharge in a frequency range of 7 MHz to 10 mHz with a 10 mV amplitude.

FIB–SEM characterization: FIB–SEM characterization was performed on an FEI Helios G4 dual-beam FIB system equipped with a Ga^+ ion beam. The consecutive slice milling and image acquisition were performed using the FEI Slice and View software. The slice thickness was 50 nm.

Image processing and reconstruction: The resulting SEM image stacks were first rescaled to compensate for the 52° angle between the electron beam and sample cross-section. Then, several representative slices were selected, and manual segmentation of different components (NMC, LPS, carbon, and void) was performed. The manually segmented images were used to train a classifier using the Trainable Weka Segmentation plug-in in the ImageJ software[2], which was then used to segment the entire image stack. All the 3D reconstruction and visualization were performed using the Dragonfly software.

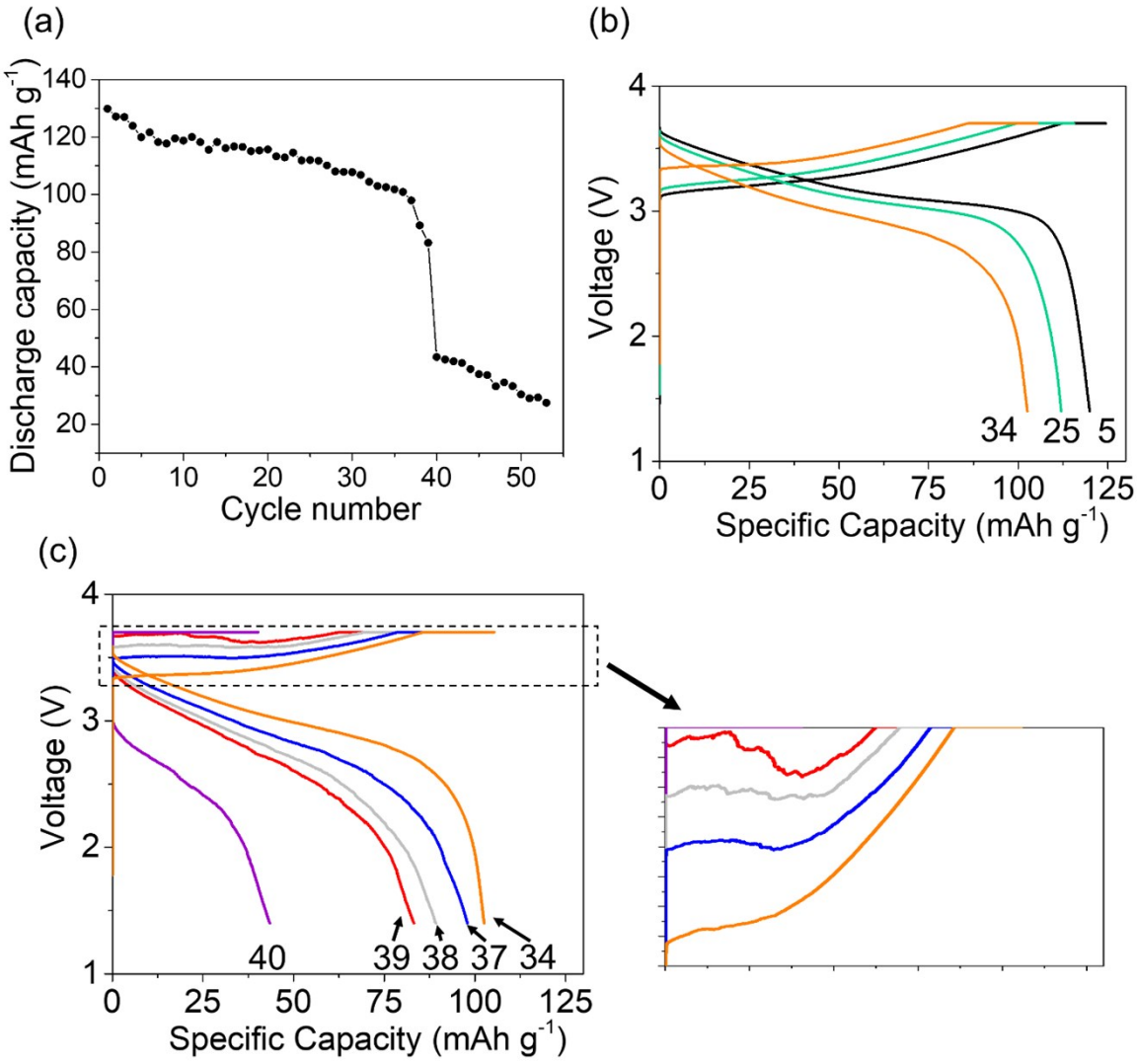

Figure S1. Electrochemical cycling results of SSB full cells. (a) Cycling performance **(b)** and **(c)** voltage profiles before and after the sudden drop in capacity. The cycling overpotential slowly increased in the first ~30 cycles, leading to gradual capacity decay, and suddenly accelerated between cycle 35 and 40. In addition, the voltage curve becomes unstable during these cycles, jumping up and down instead of smoothly increasing or decreasing (zoomed-in part of Figure S1(c)). This unstable voltage behavior can be explained by the intermittent Li transport to and from the contracting/expanding cathode particles.

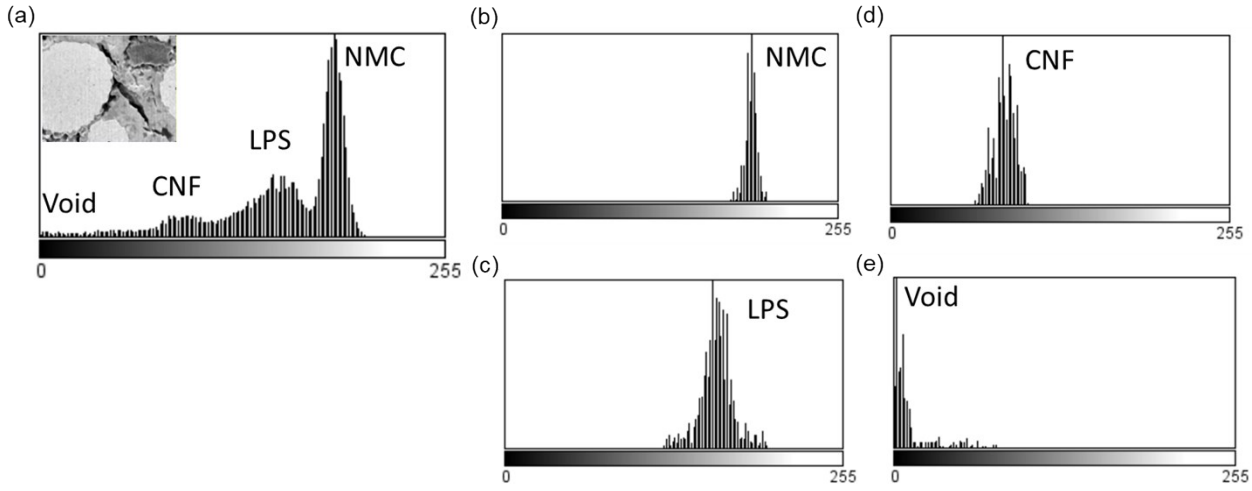

Figure S2. (a) Grayscale histogram of a backscattered electron image of the composite cathode, showing the different gray-scale of each component. Grayscale histogram extracted from the (b) NMC, (c) LPS, (d) CNF, and (e) void component, respectively. The backscattered electron image enables identification of different phases from their Z contrast with human efforts. However, image segmentation using grayscale value only was found to lead some incorrect phase identification results, especially within the boundaries of different components due to the existence of the edge effect in SEM. Therefore, a mechine learning based segementation method is used instead (Figure S3).

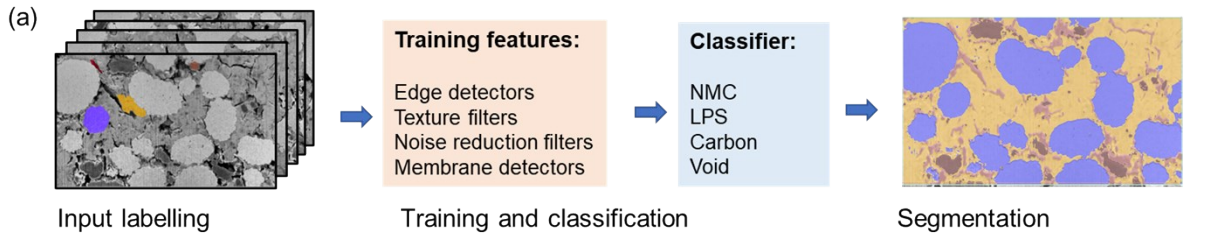

Figure S3. (a) A workflow of the image segmentation using Trainable Weka segmentation. A set of images with input pixel labelling in represented features were used to train the classifiers (NMC, LPS, carbon and void). When the classifiers were successfully trained, it were used for pixel classification for the rest of the input pixels and the whole image stack. [2] (b) Example of classification results obtained from machine learning segmentation, showing the accuracy of different phase identification.

References

(1) Ito, S., Fujiki, S., Yamada, T., Aihara, Y., Park, Y., Kim, T. Y., Baek, S., Lee, J., Doo, S.; Machida, N. A rocking chair type all-solid-state lithium ion battery adopting Li_2O–ZrO_2 coated $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and a sulfide based electrolyte. *J. Power Sources.* **2014,** *248,* 943.

(2) Arganda-Carreras, I., Kaynig, V., Rueden, C., Eliceiri, K. W., Schindelin, J., Cardona, A.; Sebastian Seung, H. Trainable Weka Segmentation: a machine learning tool for microscopy pixel classification. *Bioinformatics.* **2017,** *33,* 2424.