Supporting Information

Finding a Needle in the Haystack: Identification of Functionally Important Minority Phases in Operating Battery

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Materials and Methods

The x-ray transparent pouch cells are composed of a lithium metal anode, a Celgard separator soaked in an electrolyte of $LiPF_6$ (1 M) in ethylene carbonate and dimethyl carbonate (volume ratio 1:1), and a cathode of micrometer-sized $LiCoO_2$ (80 wt%; Alfa Aesar), carbon black (10 wt%; Chevron) and Polyvinylidene fluoride (10 wt%; Kureha). $LiCoO_2$ powder was mixed with carbon black and poly-vinylidene fluoride in N-methylpyrrolidone solvent to make a slurry. Then it was coated on Al foil and was dried under vacuum at 120 °C for 24 h. The cells were assembled inside an argon-filled glovebox and heat-sealed in polyester pouches with aluminum and copper current collectors for cathode and anode electrodes, respectively. More detailed description of the cell can be found in our earlier publication[1].

We conducted *in-situ* x-ray spectro-imaging of the cell described above using the transmission x-ray microscope at beamline 6-2C of Stanford Synchrotron Radiation Lightsource (SSRL), shown in Figure 1.a. The nominal spatial resolution of this instrument is at ~30 nm. More details of the synchrotron beamline configuration, the concept of TXM spectro-microscopy, the cell holder design can be found in other publications[1,2]. In the spectro-microscopic scan, the typical exposure time for a single image is 0.5 seconds, the energy of the incident x-rays is scanned from 7560 eV to 7980 eV with 105 energy points recorded. Over the near edge region (7700 eV to 7770 eV), we choose the energy step at 1 eV to ensure sufficient energy resolution. The pre-edge and post edge regions were scanned with energy steps of 10 eV to cover a relatively wide energy window for normalization of the spectra[3]. In this experiment, 13 field-of-views were scanned covering over 100 particles (Supplementary Figure S1). After initial data reduction, over 10

million pixel spectra were recovered. As an example, we show in Supplementary Figures S2.a and S2.b the spectrum over a selected pixel before and after normalization using a well-established method[28]. The TXM XANES data reduction and analysis is performed using an in-house developed software package known as TXM-Wizard[4].

Supplementary Figures

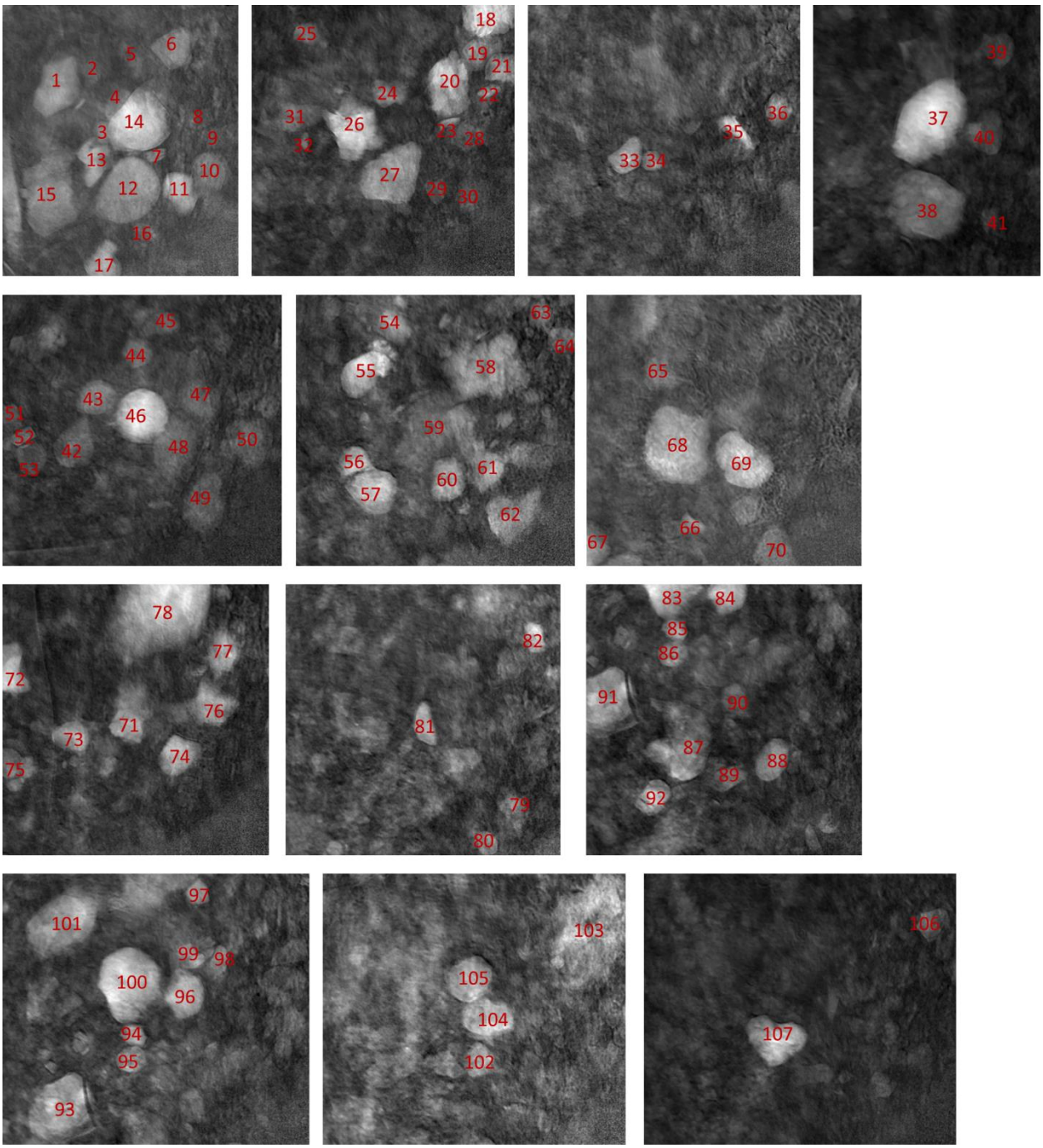

Figure S1. Transmission x-ray images of the particles surveyed in our experiment. As labeled in the images, we covered more than 100 particles with over 10 million pixel spectra. Particles no. 37 (P37) and 46 (P46) are identified as minority phases, which are investigated in more details in this work, due to their distinct spectroscopic fingerprints.

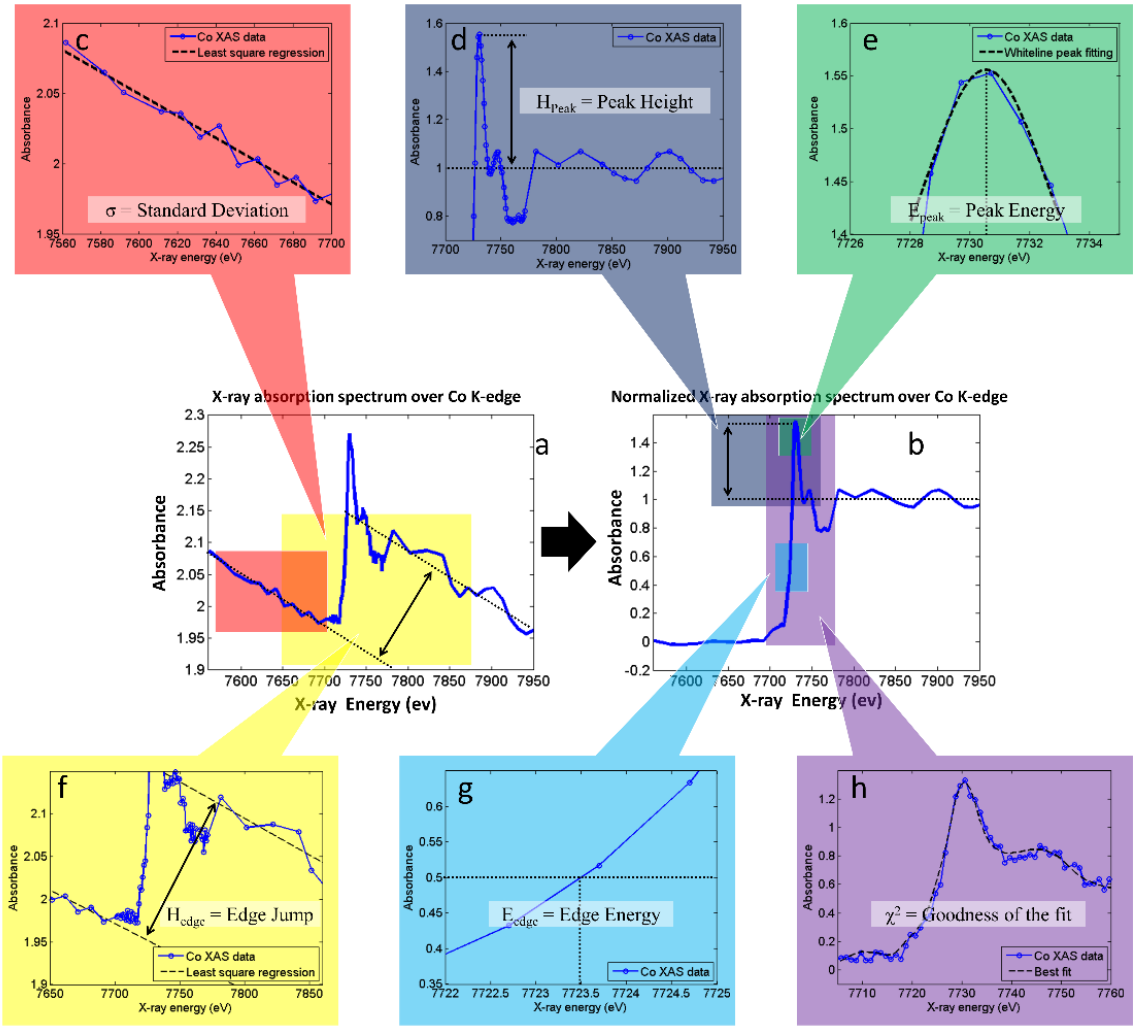

Figure S2. Data attribute extraction. The raw data of a pixel XANES is shown in panel (a) with its normalized form shown in panel (b). Panels (c) to (h) show six different data attributes we choose to extract from the spectra including (c) σ: the standard deviation of the pre-edge data with respect to the linear regression line; (d) H_{peak}: the height of the white-line peak; (e) E_{peak}: the white-line peak energy; (f) H_{edge}: the height of the edge jump; (g) E_{edge}: the edge energy, which is defined as the energy associated with the 0.5 normalized intensity; and (h) χ^2: the goodness of the linear combination fit using the two spectra of $LiCoO_2$ at charged (4.6V) and discharged (3V) states.

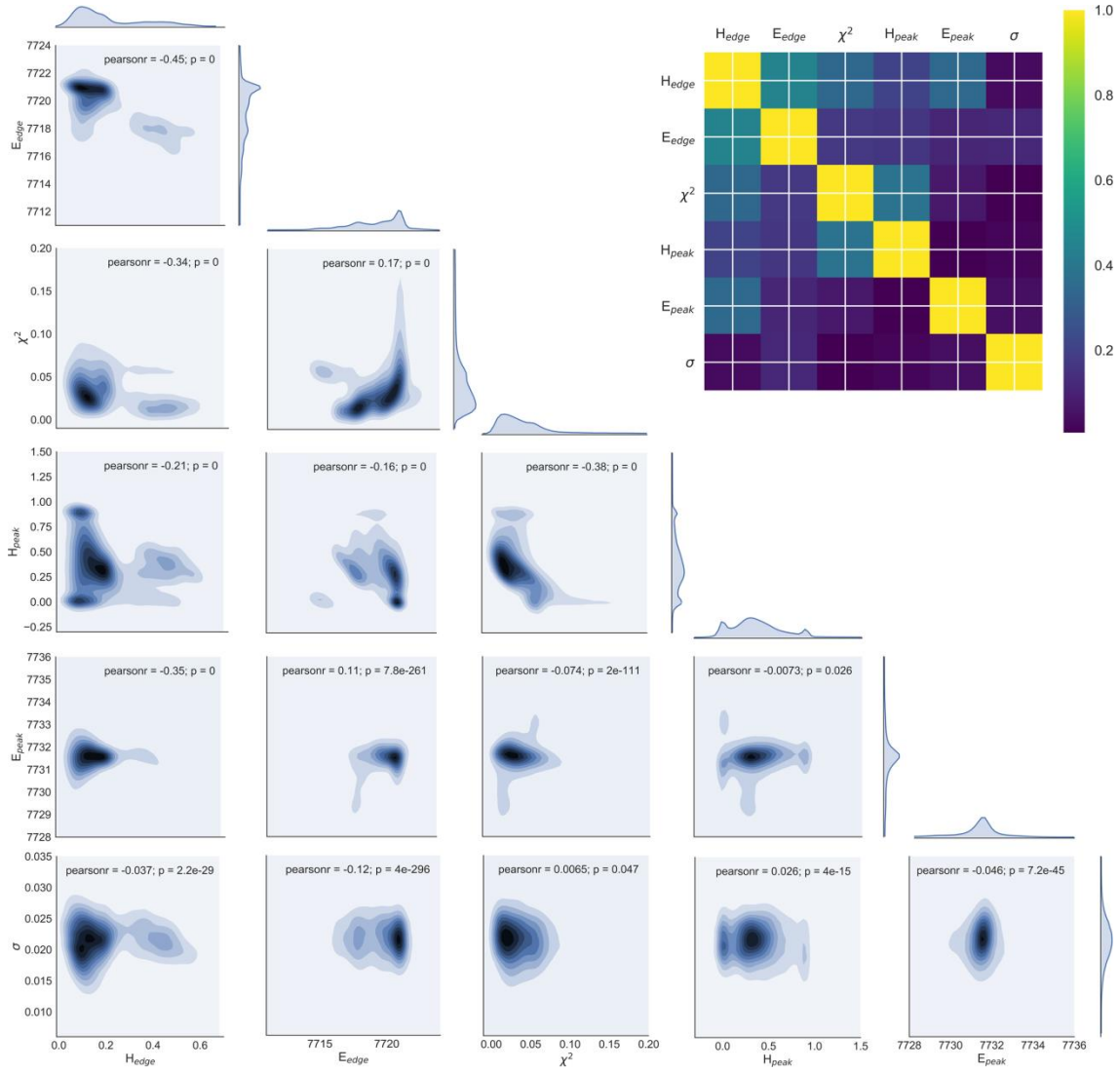

Figure S3: Bivariate analysis among the extracted key data attributes. Lower left of the figure shows the correlation plots among all the 6 extracted data attributes (supplementary Figure S2). The upper right of the figure shows the quantification of the degree of correlation by Pearson correlation coefficient (color coded to the corresponding color map).

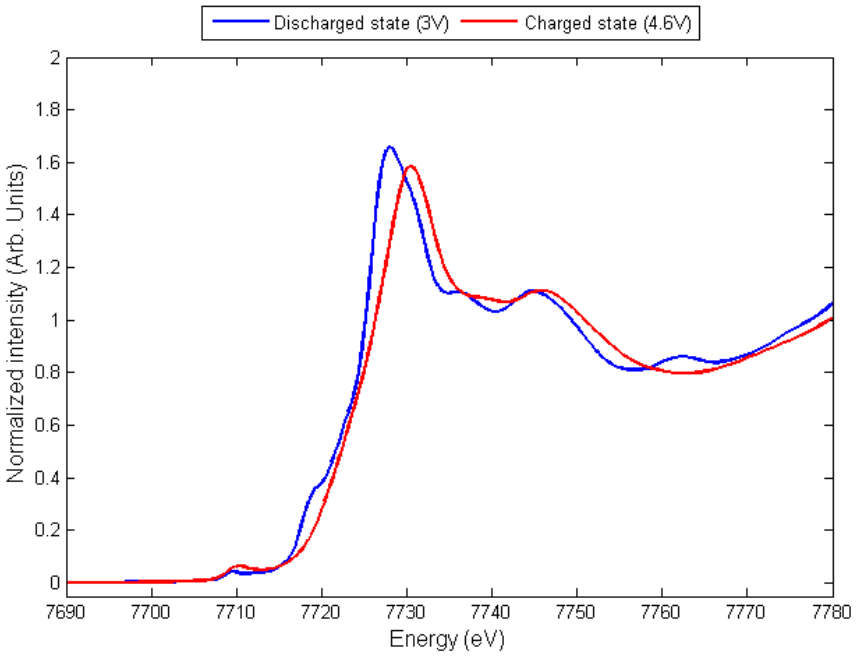

Figure S4. The standard x-ray absorption spectra of LixCoO2 at its charged state (4.6V, red) and discharged state (3V, blue).

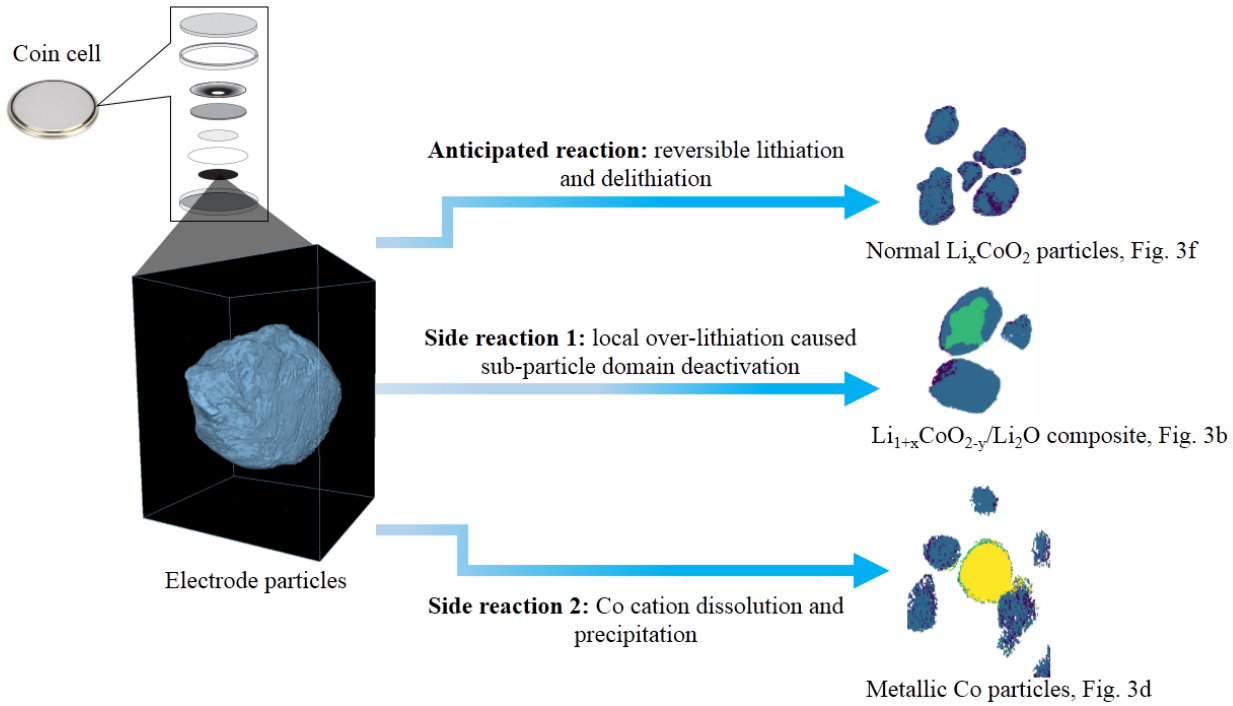

Figure S5. Schematics of the possible pathways of the anticipated and unanticipated reactions in the cell as identified by the data mining approach developed in this work.

Reference

(1) Xu, Y.; Hu, E.; Zhang, K.; Wang, X.; Borzenets, V.; Sun, Z.; Pianetta, P.; Yu, X.; Liu, Y.; Yang, X.-Q. *ACS Energy Letter* 2017, 2, 1240-1245.

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(3) Weng, T.-C.; Waldo, G. S.; Penner-Hahn, J. E. *J.Synchrotron.Radiat.* 2005, 12, 506-510.

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