

Supplementary Information for

Thermally Driven Mesoscale Chemomechanical Interplay in $\text{Li}_{0.5}\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ Cathode Materials

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Materials and methods

Material synthesis

The pristine $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NMC622) material was obtained from Argonne's Cell Analysis, Modeling and Prototyping (CAMP) Facility. The composite cathodes were prepared by spreading a slurry (N-Methyl-2-pyrrolidone as the solvent) containing active materials (NMC622, 90 wt.%), acetylene carbon (5 wt.%) and polyvinylidene difluoride (PVdF, 5 wt.%) as the binder and casting it on carbon-coated aluminum foils. The electrodes were then dried overnight at 120 °C in a vacuum oven and transferred into an Ar-filled glove box for future use. The active mass loadings for the electrodes were 8 mg/cm². CR2032 coin cells were assembled in an Ar-filled glovebox ($\text{O}_2 < 0.5$ ppm, $\text{H}_2\text{O} < 0.5$ ppm) using the composite cathode, lithium foil (MTI) as the anode, Whatman glass fiber (1827-047 934-AH) as the separator and 1M LiPF_6 dissolved in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with 2 wt.% vinylene carbonate (VC) as the electrolyte. All coin cells were cycled with an electrochemical workstation (Wuhan Land Company) at 23 °C. 1C was defined as fully charging a cathode in 1 h, corresponding to a specific current density of 200 mA/g. All the coin cells were cycled starting at C/10 for the initial cycle and then followed by a current rate of 5C. After the designated number of cycles, the coin cells were disassembled in the glovebox and the cathodes were collected for further characterizations.

Soft XAS

Soft x-ray absorption spectroscopy (XAS) measurements were carried out at the elliptically polarizing undulator (EPU) beamline 13-3 of the Stanford Synchrotron Radiation Lightsource (SSRL). The charged and heated NMC samples were mounted in an ultra-high vacuum (UHV) chamber for the measurement. The vertically polarized X-ray (sigma-polarization) was used. The incident beam was monochromatized by a 1100-lines/mm spherical grating monochromator (SGM), and its angle was set at 30 degrees from the sample surface. Both fluorescence yield (FY) and total electron yield (TEY) signals were acquired simultaneously to probe the depth-dependent spectroscopic fingerprints. All the XAS spectra were normalized by the intensity of the incoming x-ray beam that was concurrently measured as a drain current on an electrically isolated gold-coated mesh. A linear background, which was determined by the intensity of the pre-edge region, was subtracted from the data.

SEM/EDS

The NMC particles were characterized by SEM imaging using FEI Helios NanoLab 600i DualBeam FIB/SEM at the Stanford Nano Shared Facilities (SNSF). The electron accelerating voltage is 5 kV with the resolution of around 1.3 nm. The EDS spectra over regions of interest were also collected using this instrument.

TXM

In situ X-ray spectroscopic imaging of the selected particles of the charged $\text{Li}_x\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ over the Ni *K* edge were carried out using the transmission x-ray microscope at beamline 6-2c at the Stanford Synchrotron Radiation Lightsource (SSRL) of the SLAC National Accelerator Laboratory. This instrument has a nominal spatial resolution of ~30 nm. More details of the experimental setup and the descriptions of the spectroscopic imaging method can be found in the

literature [1,2]. During the spectroscopic scan, images at over 100 energy points were collected across the Ni *K* edge. The energy step in the region away from the edge energy was set to 15eV to ensure coverage of a relatively large window needed and the region near the edge energy was set to 1eV to ensure sufficient energy resolution. Data analysis was performed using an SSRL in-house developed software package known as TXM-Wizard [3].

For quantification of the morphological complexity, we show in Figure S2 the definition of the morphological complexity parameter (a dimensionless parameter defined as $\varepsilon = \frac{V^{1/3}}{S^{1/2}}$). *V* is the solid volume of the particle and *S* is the total surface area of the solid phase. As a guideline, the ε value of some standard 3D solid objects is shown in Figure S2. The smaller ε , the higher degree of morphological complexity. For a fractal dimensional object, the volume is limited but the surface area can be very large, leading to very small ε value.

Supporting Figures

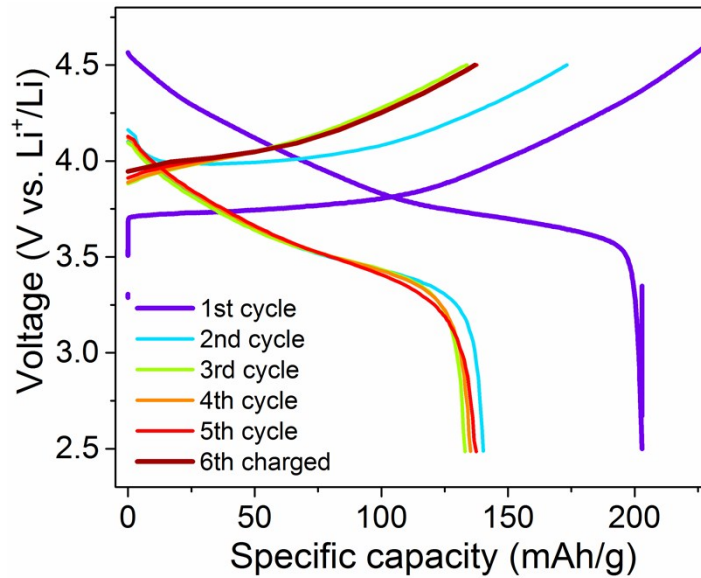


Figure S1. Cycling performance of the cell containing $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ cathode material cycled at C/10 (20 mA/g) in the range of 2.5–4.6 V for the initial cycle followed with 5C in the range of 2.5–4.5 V for 5 cycles.

	Sphere	Dodecahedron	Octahedron	Cube	tetrahedron	Particle
						
V	$\frac{4}{3}\pi R^3$	$\frac{1}{4}(15+7\sqrt{5})R^3$	$\frac{1}{3}\sqrt{2}R^3$	R^3	$\frac{1}{12}\sqrt{2}R^3$	
S	$4\pi R^2$	$3\sqrt{25+10\sqrt{5}}R^2$	$2\sqrt{3}R^2$	$6R^2$	$\sqrt{3}R^2$	
$\varepsilon = \frac{V^{1/3}}{S^{1/2}}$	0.4547	0.4339	0.4182	0.4082	0.3725	Depends

Figure S2. The definition of the morphological complexity, which was a dimensionless parameter defined as $\varepsilon = \frac{V^{1/3}}{S^{1/2}}$. V is the solid volume of the particle and S is the total surface area of the solid phase. As a guideline, the ε value of some standard 3D solid objects is shown here. For a fractal dimensional object, the volume is limited but the surface area can be very large, leading to very small ε value.

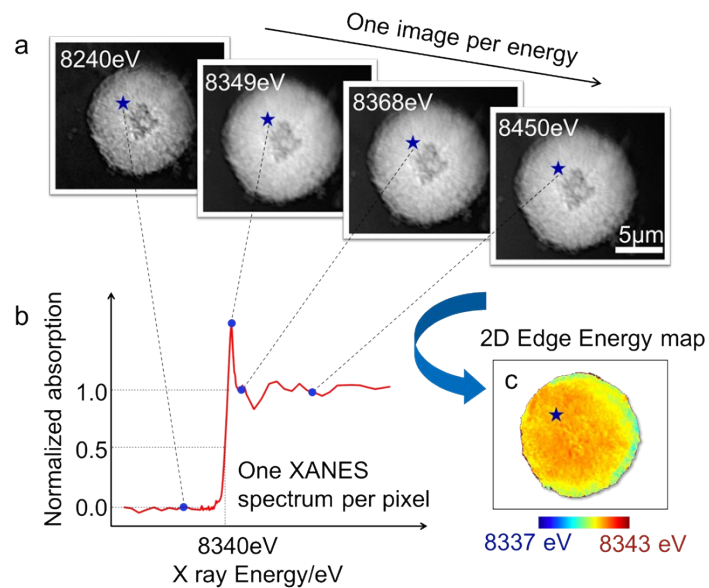


Figure S3. Illustration of extracting 2D mesoscale chemical heterogeneity from the full-field X ray spectro-microscopy data. Panel (a) illustrates the data structure, which is a sequence of projective images collected using the transmission X ray microscopy at different energies. Panel (b) is one XANES spectrum from a selected pixel. Panel (c) is relative oxidation state map, which is color coded to the edge energy defined as the X ray energy that corresponds to the normalized absorption value at 0.5.

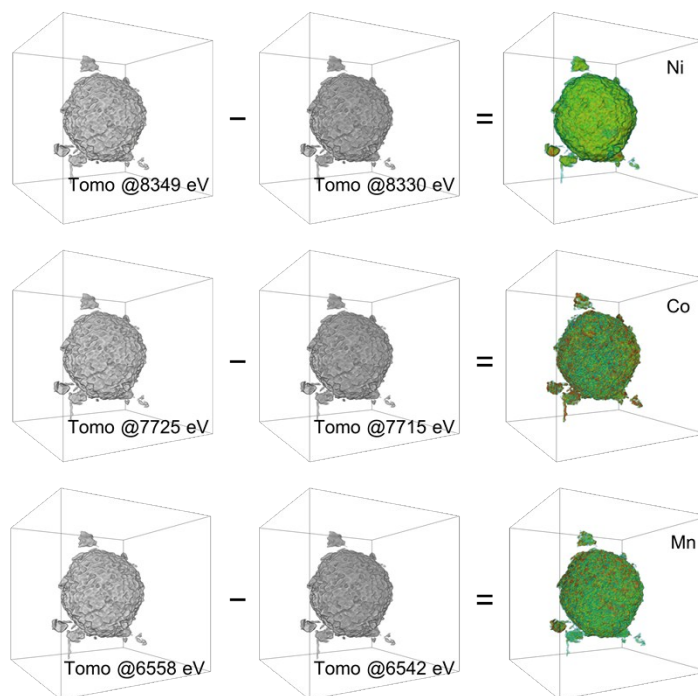


Figure S4. Illustration of the 3D elemental distribution resolved from tomography results above and below the K-edges of Mn, Co and Ni. The differential contrast above and below the absorption edges is proportional to the corresponding elemental concentration.

Reference

- [1] Y. Liu, F. Meirer, P.A. Williams, J. Wang, J.C. Andrews, P. Pianetta, *TXM-Wizard*: a program for advanced data collection and evaluation in full-field transmission X-ray microscopy, *Journal of Synchrotron Radiation*. 19 (2012) 281–287.
- [2] F. Meirer, J. Cabana, Y. Liu, A. Mehta, J.C. Andrews, P. Pianetta, Three-dimensional imaging of chemical phase transformations at the nanoscale with full-field transmission X-ray microscopy, *Journal of Synchrotron Radiation*. 18 (2011) 773–781.

- [3] Y. Liu, F. Meirer, J. Wang, G. Requena, P. Williams, J. Nelson, A. Mehta, J.C. Andrews, P. Pianetta, 3D elemental sensitive imaging using transmission X-ray microscopy, *Analytical and Bioanalytical Chemistry*. 404 (2012) 1297–1301.
- [4] C. Wei, S. Xia, H. Huang, Y. Mao, P. Pianetta and Y. Liu, *Accounts of Chemical Research*, 2018, DOI:10.1021/acs.accounts.8b00123.
- [5] T.L. Kao, C.Y. Shi, J. Wang, W.L. Mao, Y. Liu, W. Yang, Nanoscale elemental sensitivity study of $\text{Nd}_2\text{Fe}_{14}\text{B}$ using absorption correlation tomography, *Microscopy Research and Technique*. 76 (2013) 1112–1117.