

Ultrastable cathodes enabled by compositional and structural dual-gradient design

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Supplementary information

Ultrastable Cathodes Enabled by Composition and Structure Dual-Gradient Design

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Supplementary Table 1. The refinement results of the HEXRD measurements of SCDG, FCG and NMC, including lattice parameters, Li/Ni disorder and R_{wp} .

Samples	a=b	c	Li/Ni disorder	R_{wp}
SCDG	2.8710	14.1995	3.89%	0.0746
FCG	2.8705	14.1943	2.67%	0.0655
NMC	2.8704	14.2054	2.70%	0.0632

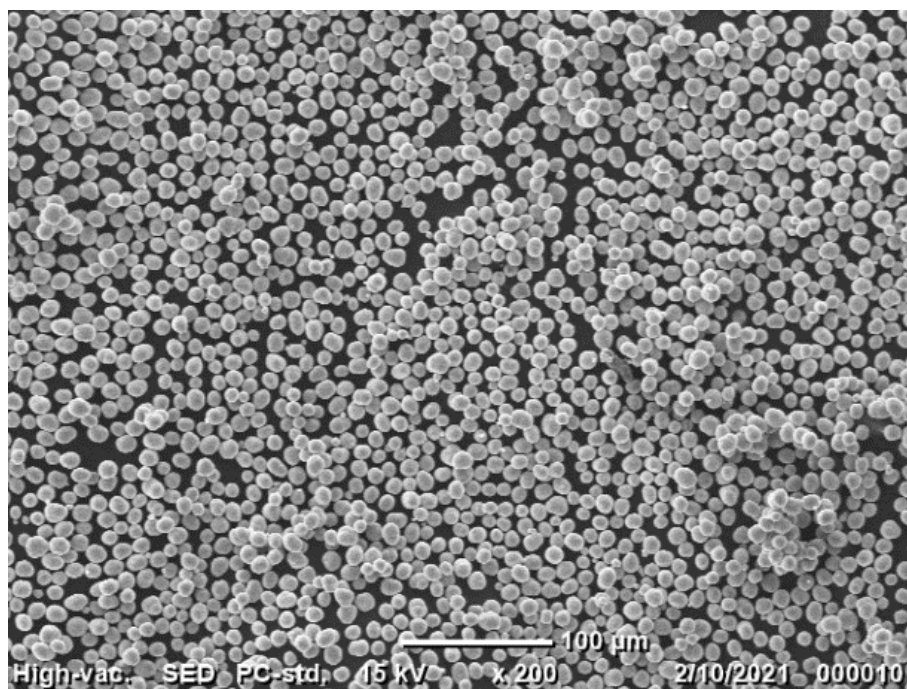
SCDG: structure ordering/concentration dual-gradient; FCG: full concentration gradient; NMC: conventional $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$.

Supplementary Table 2. The inductively coupled plasma-atomic emission spectrometry results of the structure ordering and concentration dual gradient cathode (SCDG). All element contents are normalized with the nickel content.

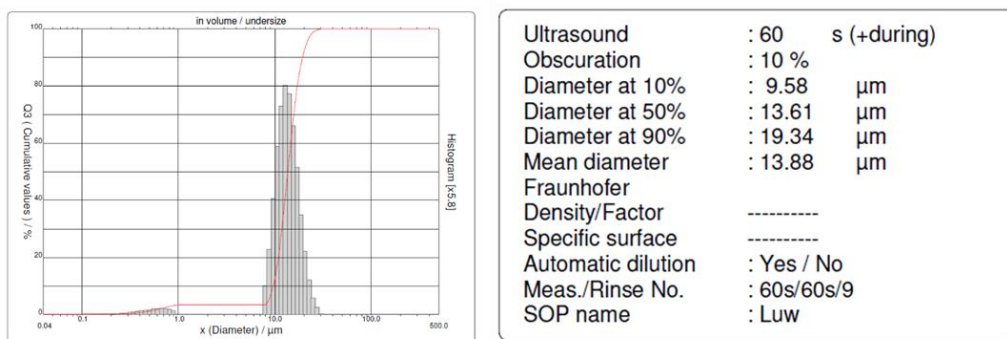
Samples	Li	Ni	Mn	Co
SCDG	1.015	0.821	0.102	0.077

Supplementary Table 3 The quantitative analysis of transition metals dissolution of NMC and SCDG.

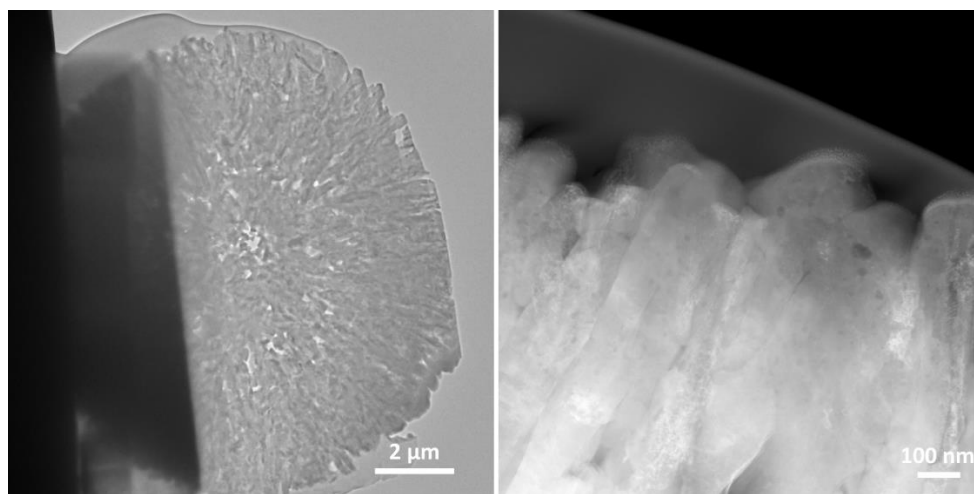
Sample name	Co(ug/cm ²)	Mn(ug/cm ²)	Ni(ug/cm ²)
NMC	0.09887 ± 0.0225	0.4457 ± 0.0522	1.3582 ± 0.2798
SCDG	0.05992 ± 0.0146	0.2018 ± 0.0329	0.6785 ± 0.1528



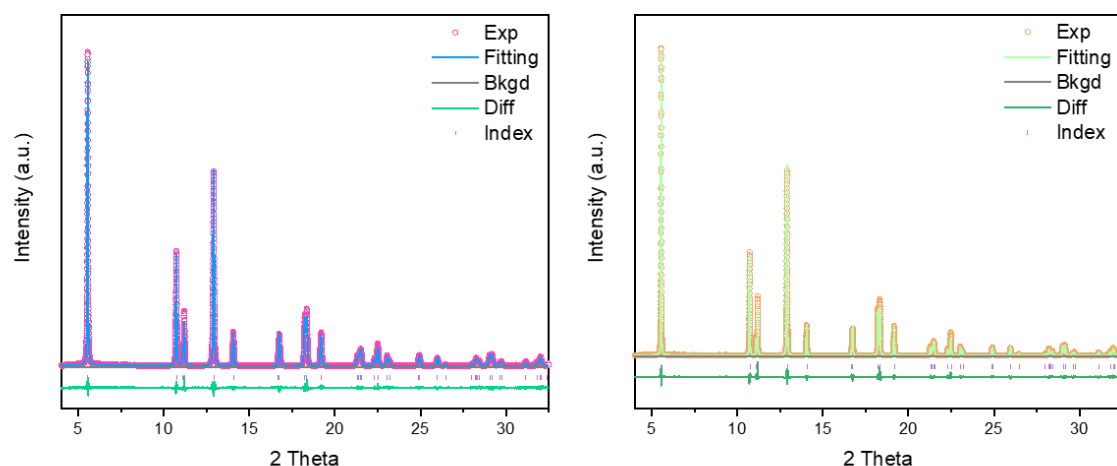
Supplementary Figure 1. The morphology measurements of the SCDG cathode using SEM.



Supplementary Figure 2. The particle size distribution of the SCDG cathode based on Particle Size Analyser result. The D50 of the SCDG is 13.61 μm.

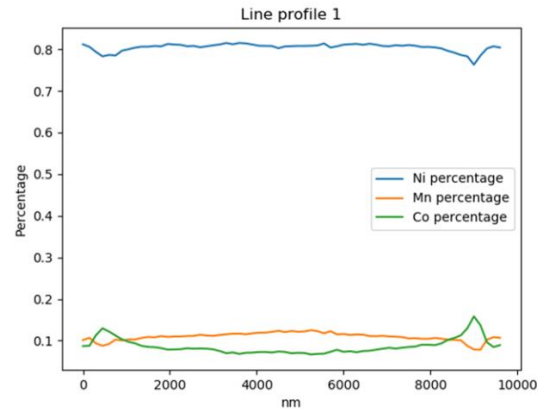
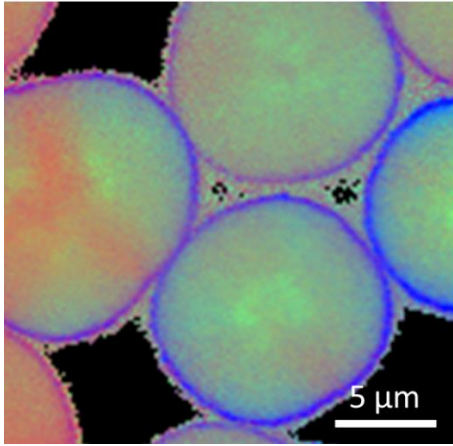


Supplementary Figure 3 Low/high magnification of TEM and STEM images of the SCDG cross-section sample. These images clearly show that the secondary particle of SCDG is composed of densely packed primary particles with rod shape.

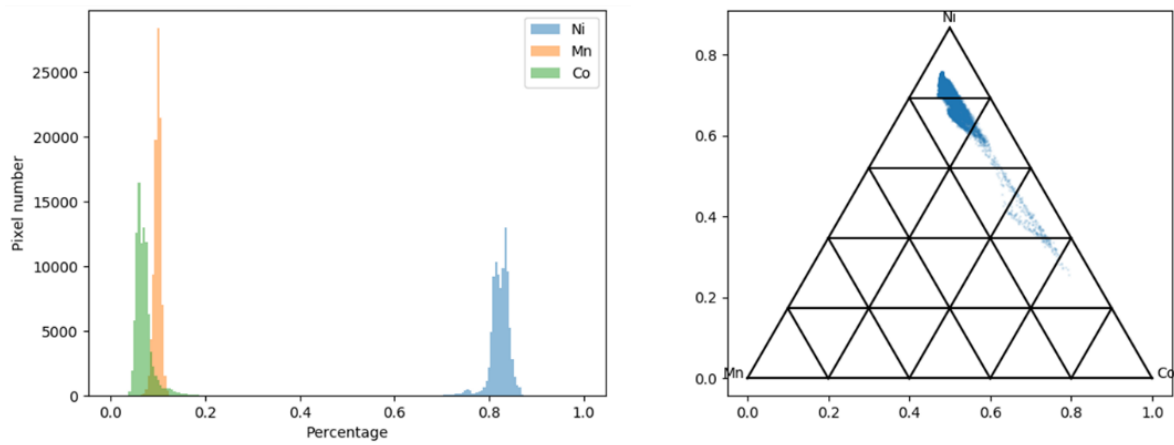


Supplementary Figure 4. High-resolution synchrotron based XRD and Rietveld refinements for full concentration gradient $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (FCG) (left) and conventional $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC) cathodes (right).

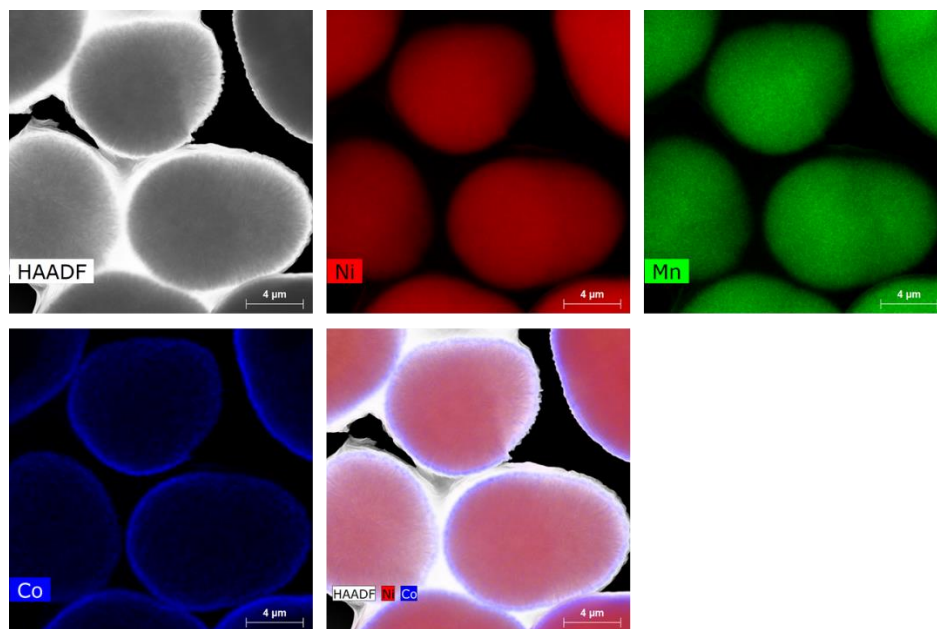
High-resolution synchrotron-based XRD (HRXRD) was conducted to investigate the effects of various composition designs on the initial structure of as-prepared cathodes. The XRD patterns with Rietveld refinements of as-prepared samples not only exhibit the characteristic Bragg peaks for a well-crystallized NaFeO_2 structure with $R-3m$ symmetry but also some differences in structural features, such as the lattice parameters and atomic occupancies. In [Supplementary Table 1](#), the refinement results illustrate a slight difference in Li/Ni disorder among samples. The SCDG sample shows a bit higher content of Li/Ni disorder because we build up a disorder outer-layer near the surface.



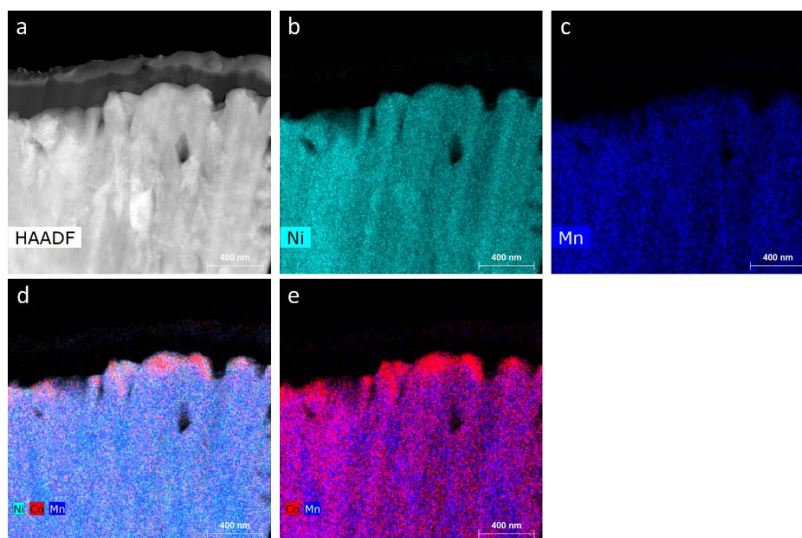
Supplementary Figure 5. The compositional measurements of the SCDG cathode using 2D X-ray fluorescence.



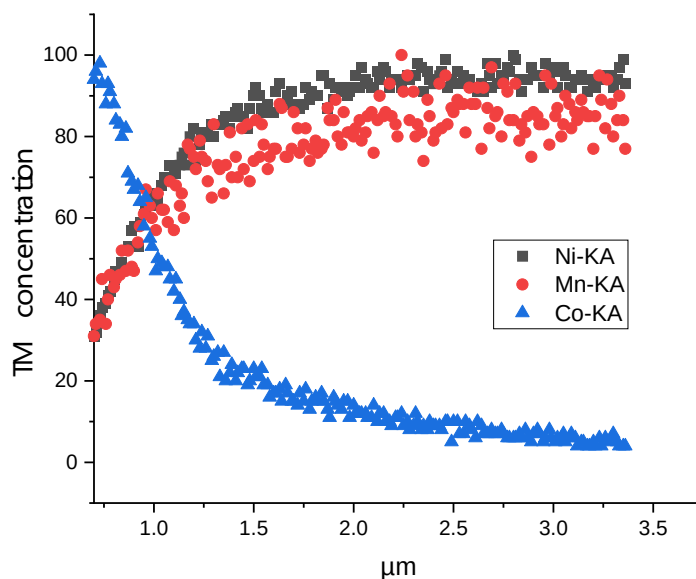
Supplementary Figure 6. The statistical compositional measurements of the SCDG cathode using 2D X-ray fluorescence.



Supplementary Figure 7. The compositional measurements of the SCDG cathode using STEM-EDS mapping.

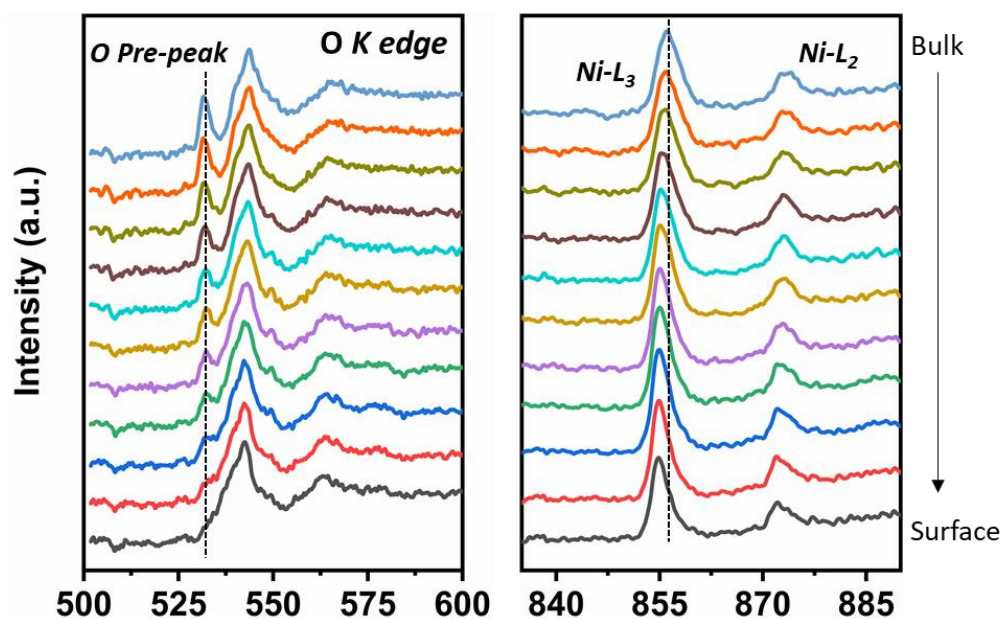


Supplementary Figure 8. The EDS mapping of the cross-section of the SCDG particle surface. **a** HAADF image, **b** Ni, **c** Mn, **d** Ni+Co+Mn, **e** Co+Mn elements mapping of the SCDG particle surface.



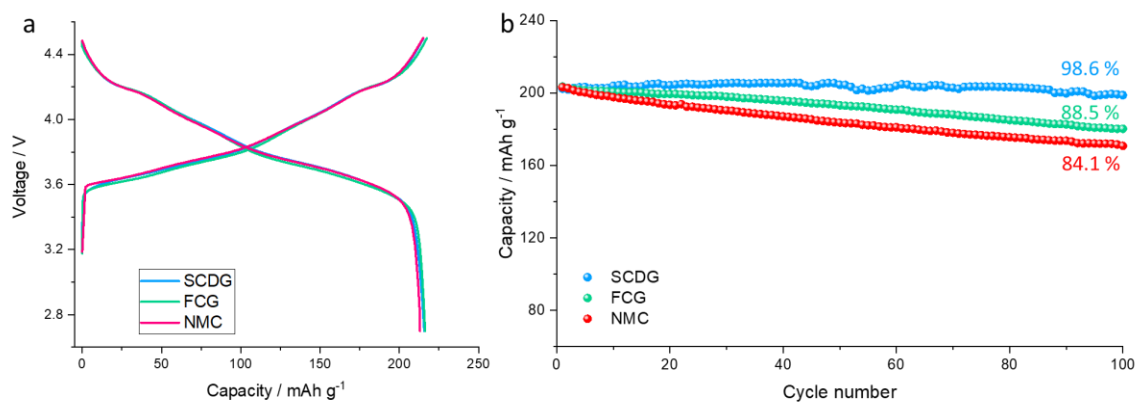
Supplementary Figure 9. The line-profile of EDX mapping of SCDG cathode. The TM concentrations of Ni, Mn and Co has normalized individually.

Compositions and morphologies of the SCDG were initially analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Scanning Electron Microscope (SEM), Particle Size Analyser and 2D/3D X-ray fluorescence. Data in [Supplementary Table 2](#) confirms that the composition of as-prepared sample was extremely close to the designed composition. [Supplementary Figure 1](#) shows that the SCDG cathode has high morphological uniformity with an average particle size of 13 μm, which is consistent with the D50 of the PSA result in [Supplementary Figure 2](#). The statistical composition of the SCDG particle clearly shows the average composition is around 82% Ni, 10% Mn and 8% Co, which is in line with the ICP results. ([Supplementary Figure 6](#))

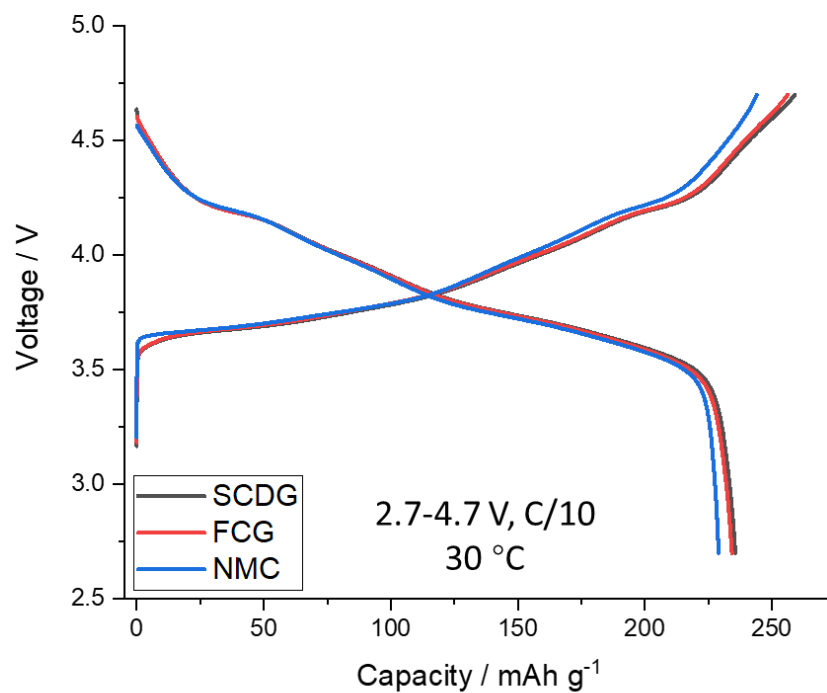


Supplementary Figure 10. EELS line-scan of the pristine SCDG surface. The pre-peak of O *K*-edge gradually decreases and *L*-edge of Ni continuously shifts left toward surface.

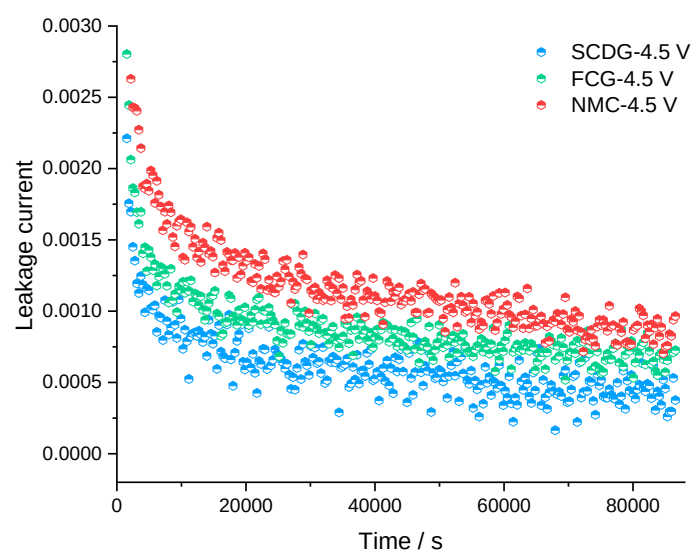
The reduction in Ni valence and concentration plays a crucial role in minimizing parasitic side reactions during high-voltage charging. This not only enhances the structural robustness of the cathode materials but also contributes to an overall improvement in battery performance. We have incorporated this discussion in the revised manuscript.



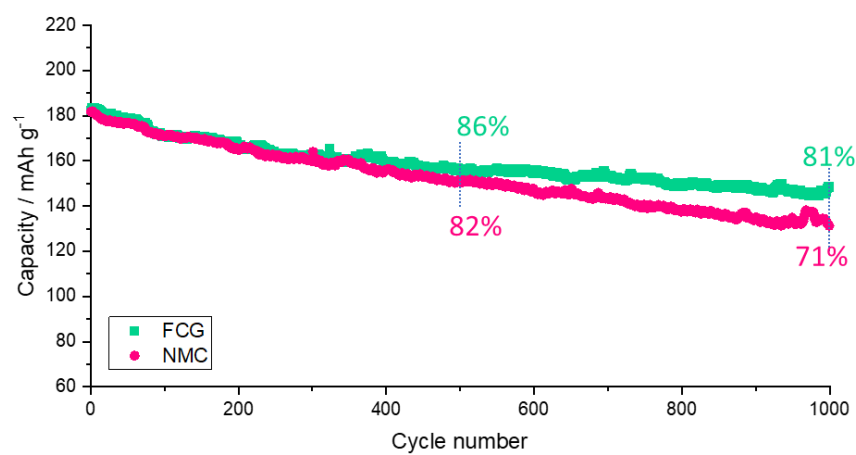
Supplementary Figure 11. Charge/discharge curves of SCDG, FCG and NMC with voltage ranges of 2.7-4.5 V at the rate of 0.1C at room temperature ($22 \pm 0.5^\circ\text{C}$). b. Cycle performance of these comparable samples at a current rate of 0.5C with a cutoff voltage of 4.5 V at room temperature (30°C).



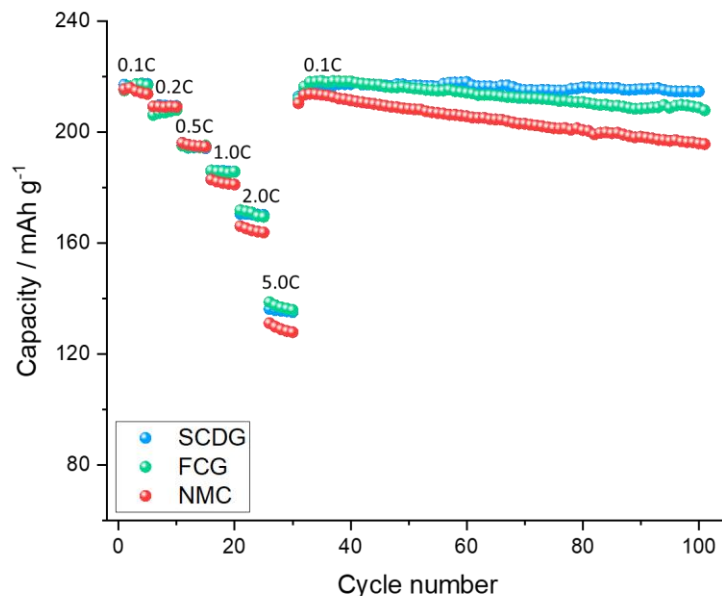
Supplementary Figure 12. Charge/discharge curves of SCDG, FCG and NMC with voltage ranges of 2.7-4.7 V at the rate of 0.1C at 30 °C.



Supplementary Figure 13 Leakage current measurements at 4.5V of the as-prepared samples at 30 °C.

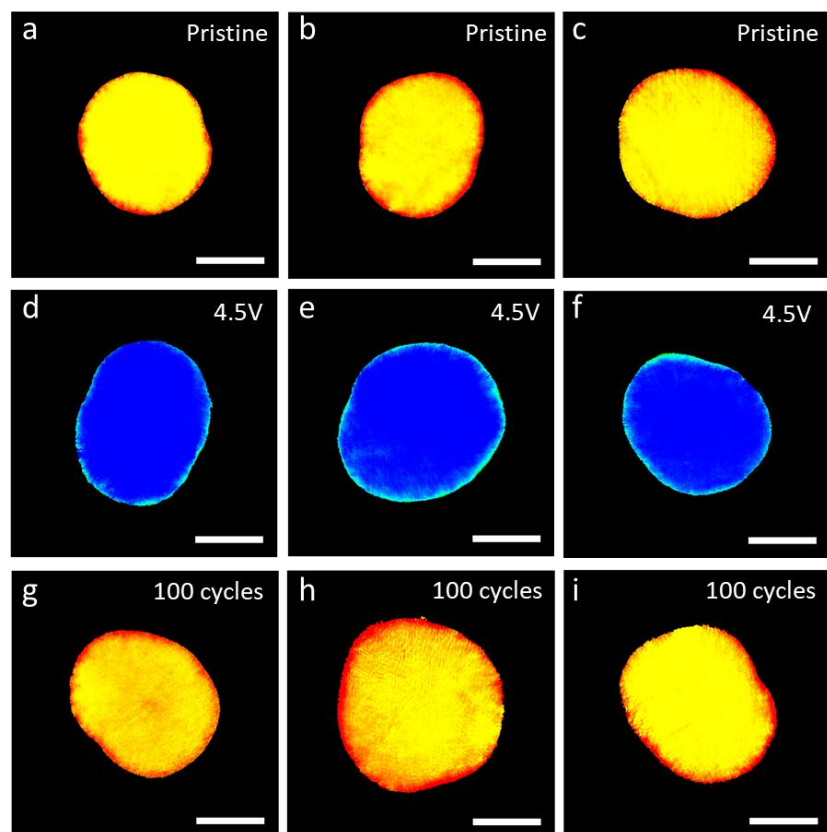


Supplementary Figure 14. Cycle performance comparison of FCG and NMC full cell at a rate of 1 C within a voltage range of 2.7-4.35 V.

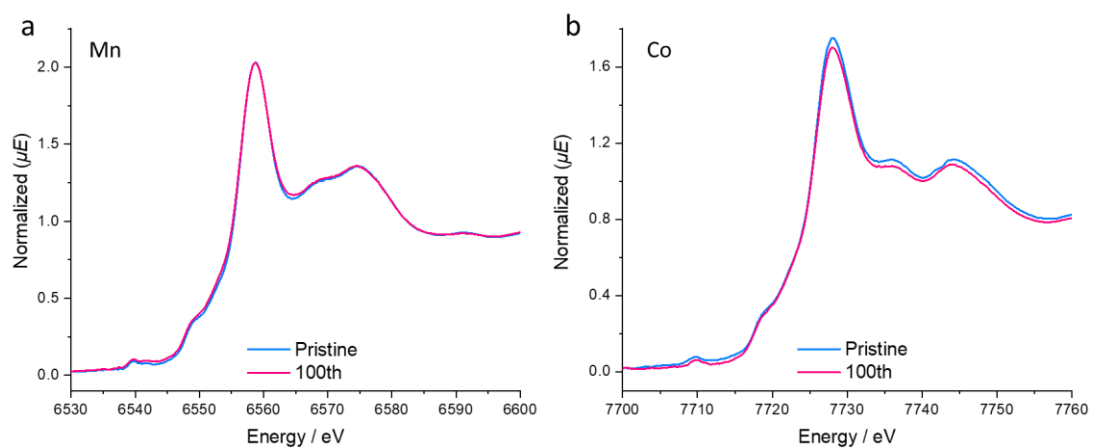


Supplementary Figure 15. The rate capabilities of SCDG, FCG and NMC cathodes.

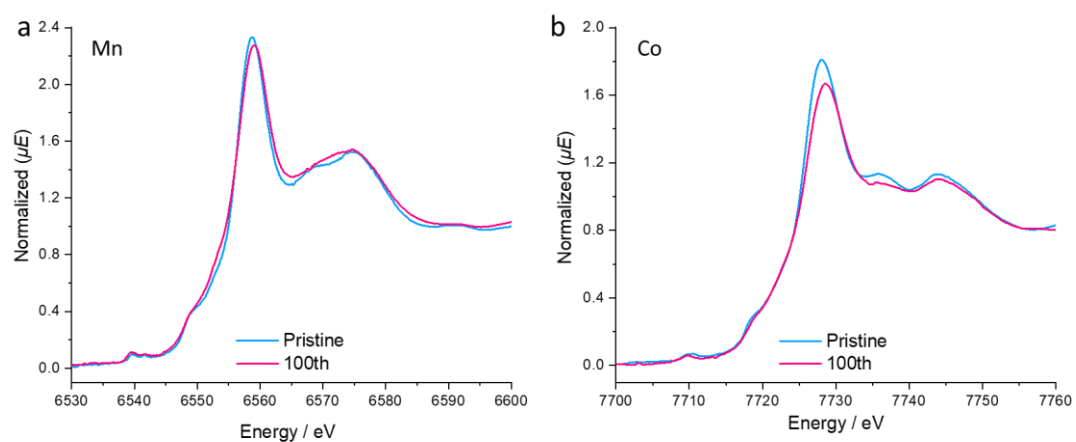
Generally, the introduction of the disordered structure barely affects the rate capability. This is attributed to the disordered phase is only being present on the tip of the surface primary particles. Additionally, the primary particles are designed in a needle shape which minimizes lattice strain and accelerates Li^+ intercalation kinetics. As shown in **Supplementary Figure 15**, SCDG and FCG show similar rate capabilities and their capacities are recoverable when the rate decreases to 0.1 C. In contrast, NMC cathode show a decreased rate capability at high rates and an obvious capacity drop when the rate decreases to 0.1 C. This is likely due to the surface structural damage that occurs during low-rate cycles. Note that after rate capability tests, SCDG can still cycle very well with negligible capacity loss, while FCG and NMC show capacity degradation.



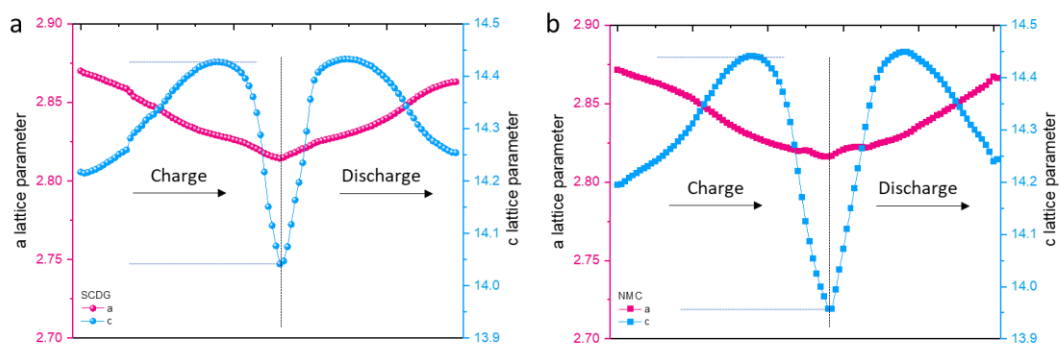
Supplementary Figure 16. **a-c** 2D TXM XANES images of pristine particles. **d-f** 2D TXM XANES images of charged particles at 4.5V. **g-i** 2D TXM XANES images of cycled particles after 100 cycles. scale bar: 5 μm .



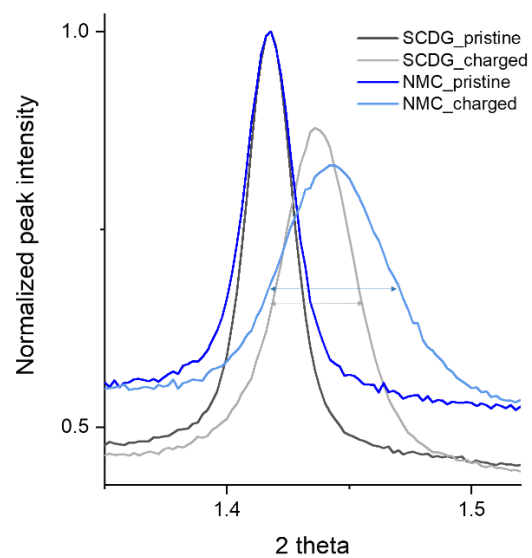
Supplementary Figure 17. *Ex-situ* Mn *K*-edge and Co *K*-edge XANES spectra of SCDG at pristine state and after 100 cycles.



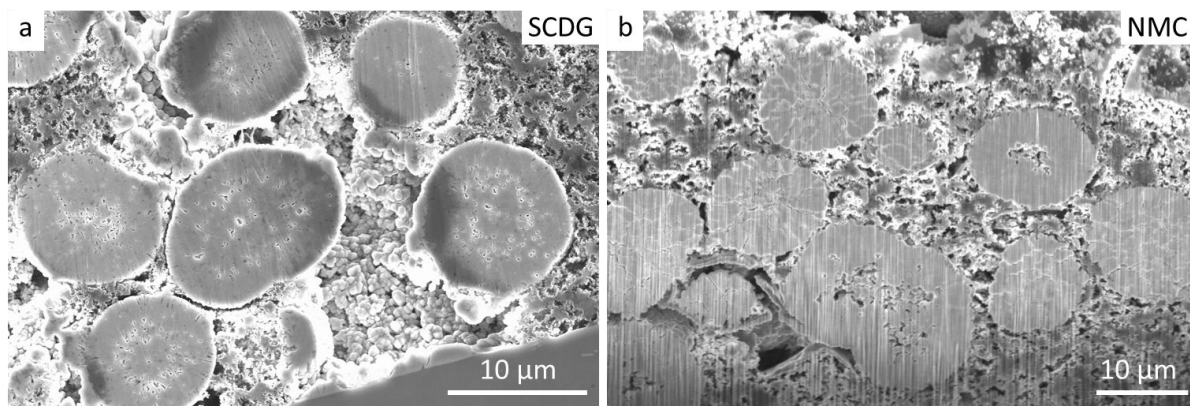
Supplementary Figure 18. *Ex-situ* Mn *K*-edge and Co *K*-edge XANES spectra of NMC at pristine state and after 100 cycles.



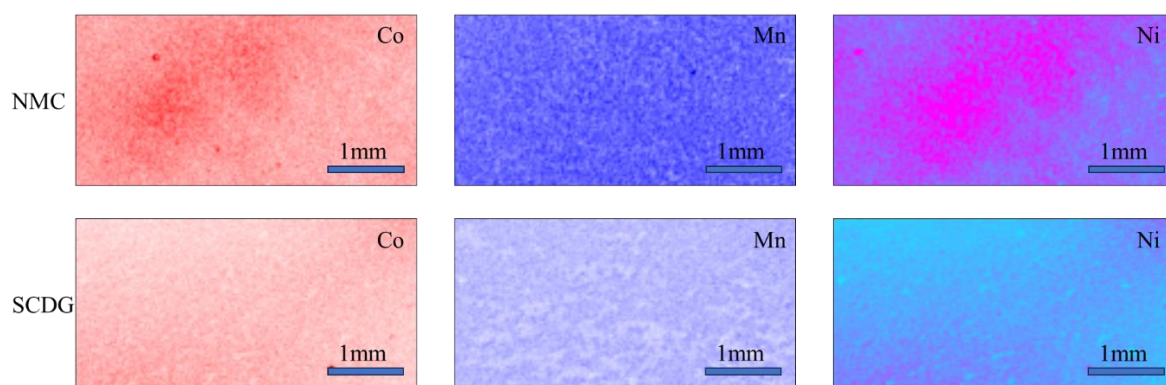
Supplementary Figure 19. a and b The quantitative analysis of in-situ XRD of SCDG and NMC based on Rietveld refinements.



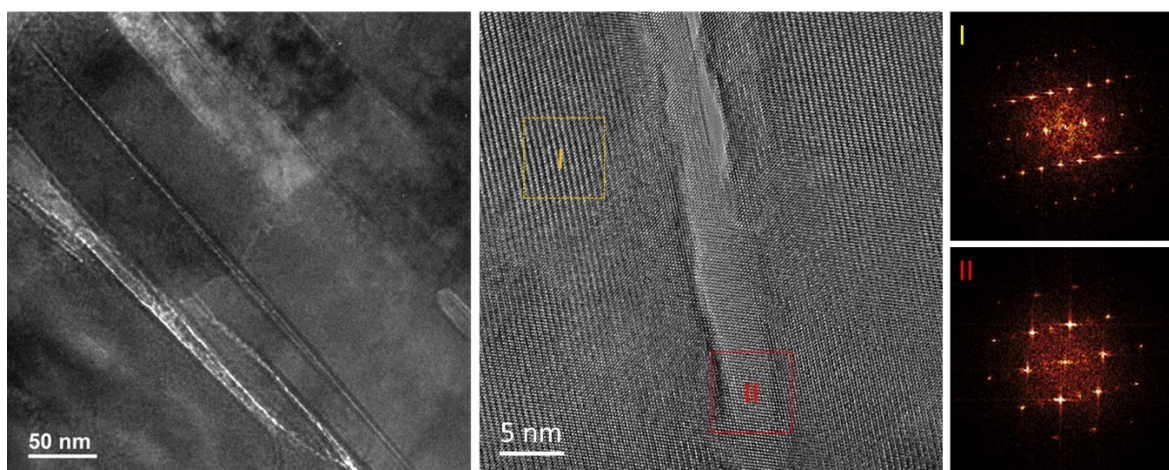
Supplementary Figure 20. The XRD patterns of pristine and charged NMC and SCDG electrodes.



Supplementary Figure 21. The cross-section images of the cycled SCDG and NMC electrodes.



Supplementary Figure 22. Transition metal dissolution of NMC and SCDG measured by 2D X-ray fluorescence. Plotting scale: all images show a 4.5mm * 2.25mm area of samples. Co: white to red 0-1, Mn: white to blue 0-1, Ni: cyan to purple 0-5.



Supplementary Figure 23 Ex situ postmortem low magnification TEM images of NMC particle after 100 cycle at a rate of $C/2$. Particle cracks occur in the particle interior and particle surface area. Surface side reactions occurred along with particle cracking with the generation of inactive rock-salt phase.