Electronic Supplementary Information (ESI)

Cation ordering Ni-rich layered cathode for ultra-long battery life

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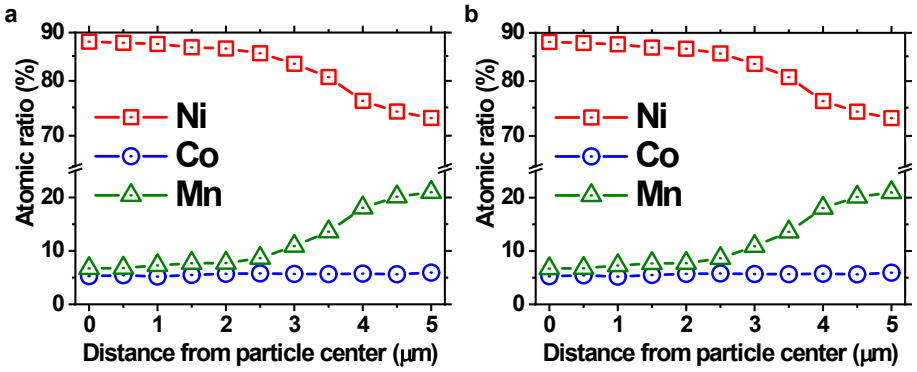

Fig. S1 EPMA compositional scan across the (a) GC80 and (b) F-GC80 lithiated particle.

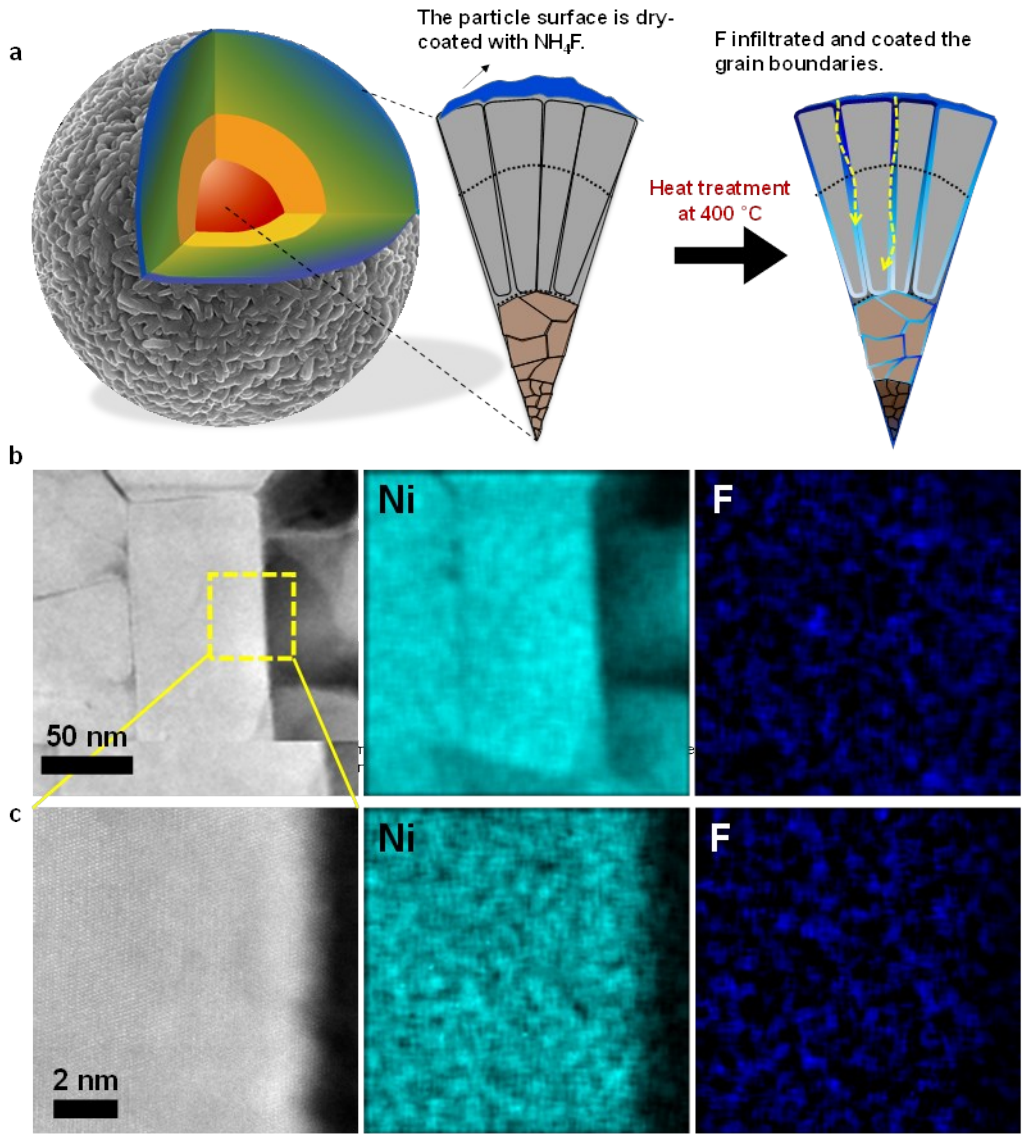

Fig. S2 (a) Schematic image showing the infiltration of F following the heat treatment. (b), (c) EDS mapping of Ni and F of the F-doped GC80 cathode.

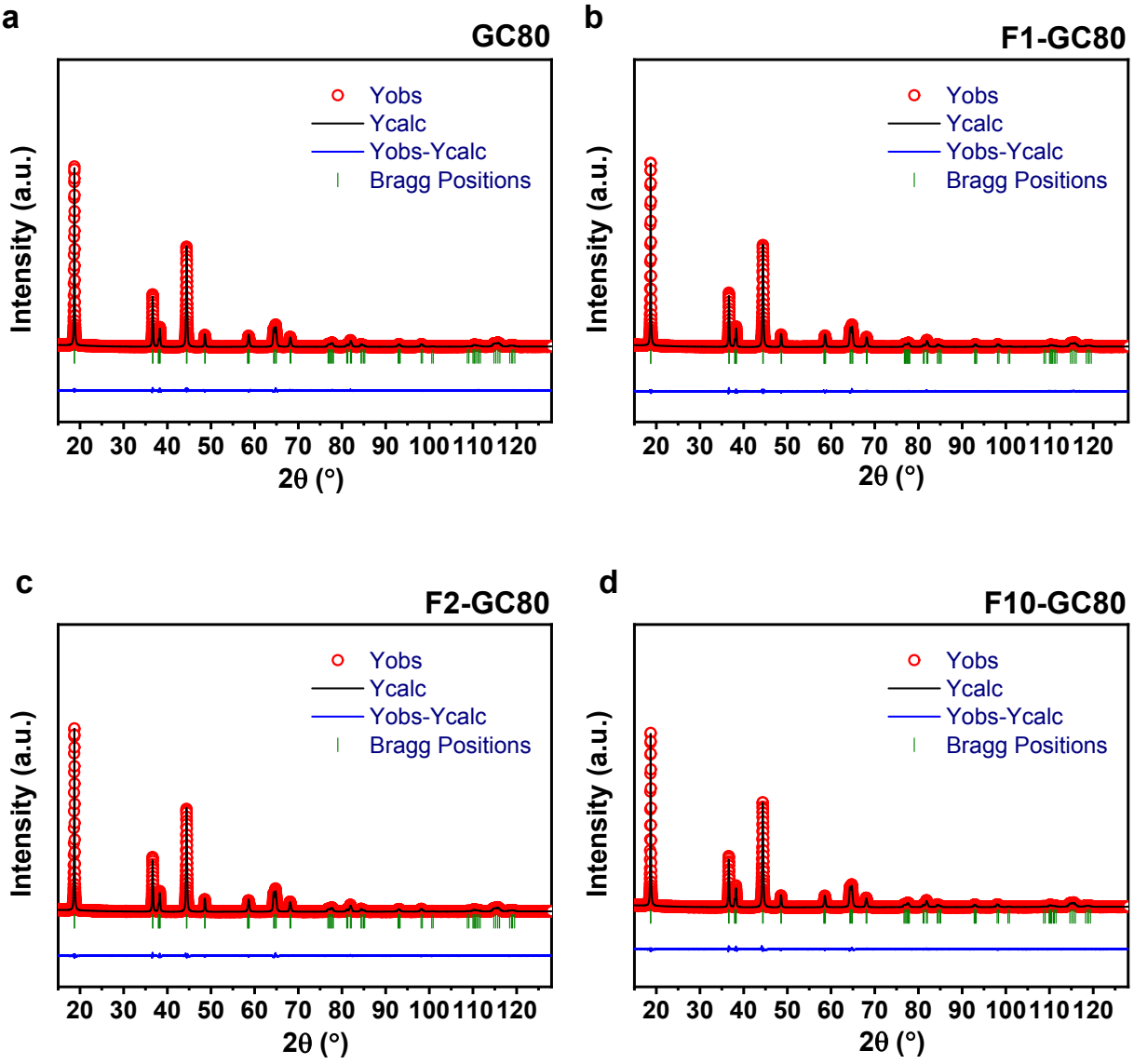

Fig. S3 Rietveld refinement result for the XRD data for (a) GC80, (b) F1-GC80, (c) F2-GC80, and (d) F10-GC80.

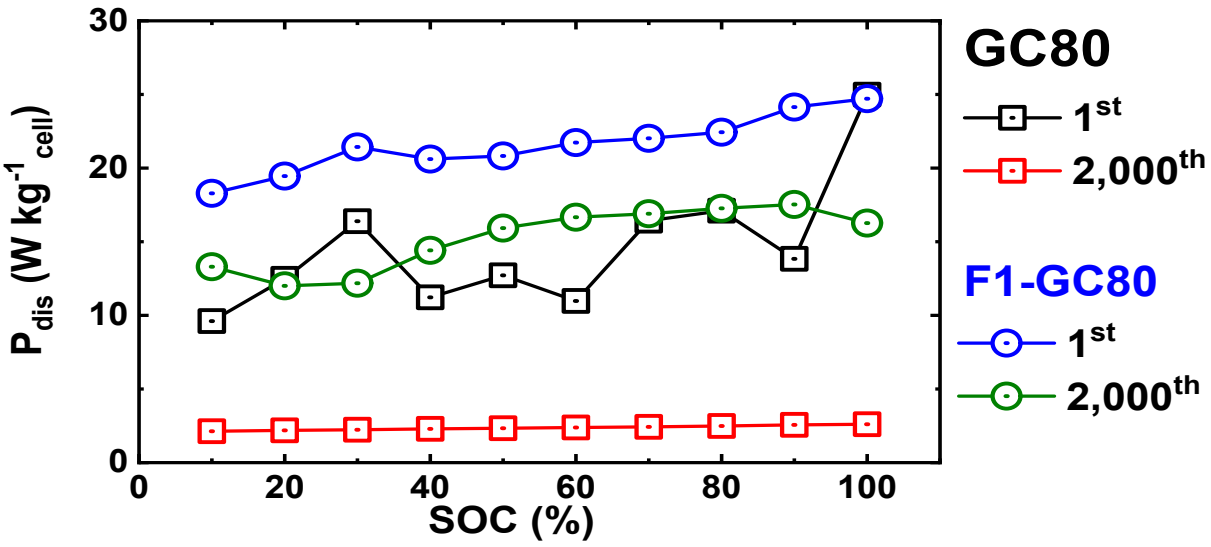

Fig. S4 Hybrid pulse power characterization (HPPC) test for GC80 and F1-GC80. Power as a function of various states of charge for each cycle numbers.

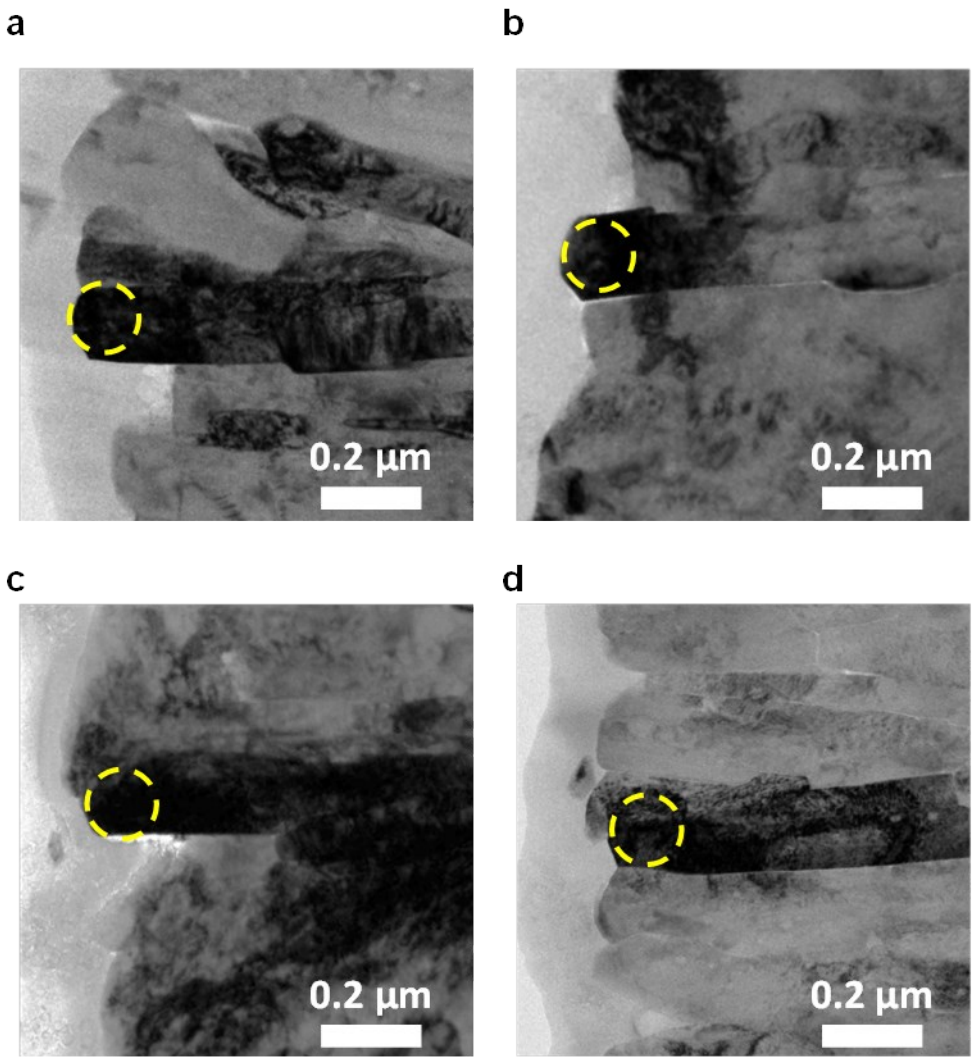

Fig. S5 High-magnification TEM image of the surface for F1-GC80: (a) As-prepared, (b) charged to 4.3V, (c) after 20 cycle (discharged state), and (d) after 2,000 cycle (discharged state).

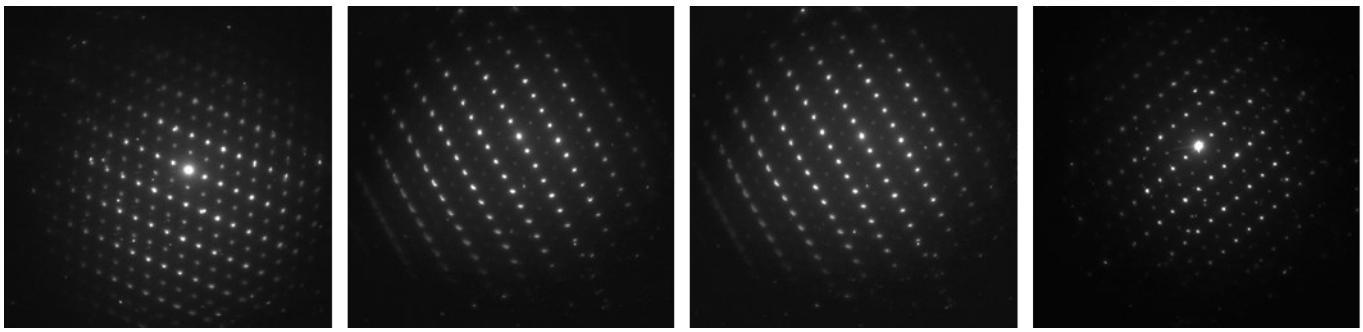

Fig. S6 [100] zone SAED patterns of the F1-GC80 cathode after 5000 cycles from different primary particles showing extra superlattice diffraction spots.

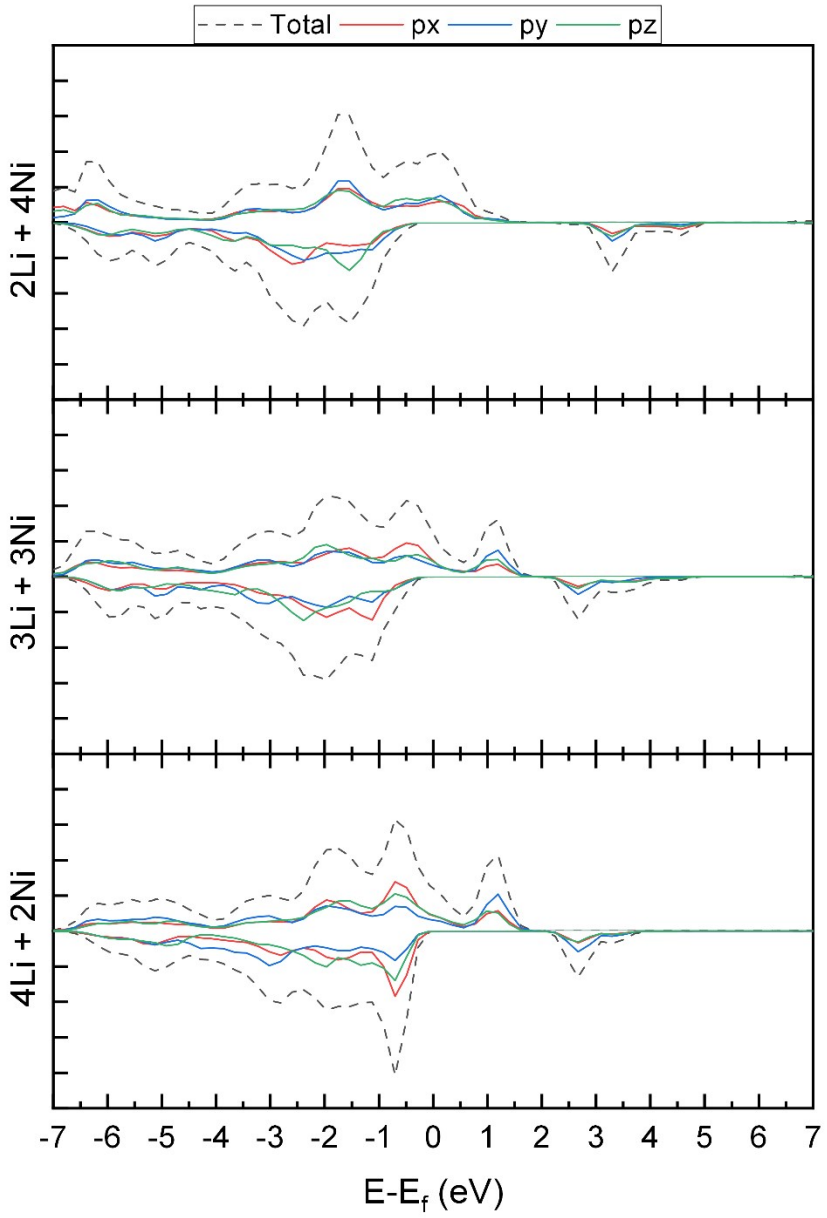

Fig. S7 Density of states of a single octahedrally coordinated oxygen atom. Each of the three panels shows a different coordination configuration for an octahedrally coordinated oxygen ion in $LiNiO_2$. All three coordination complexes can be found in the ordered structure, but only the "stoichiometric" case (middle panel) exists in the layered structure.

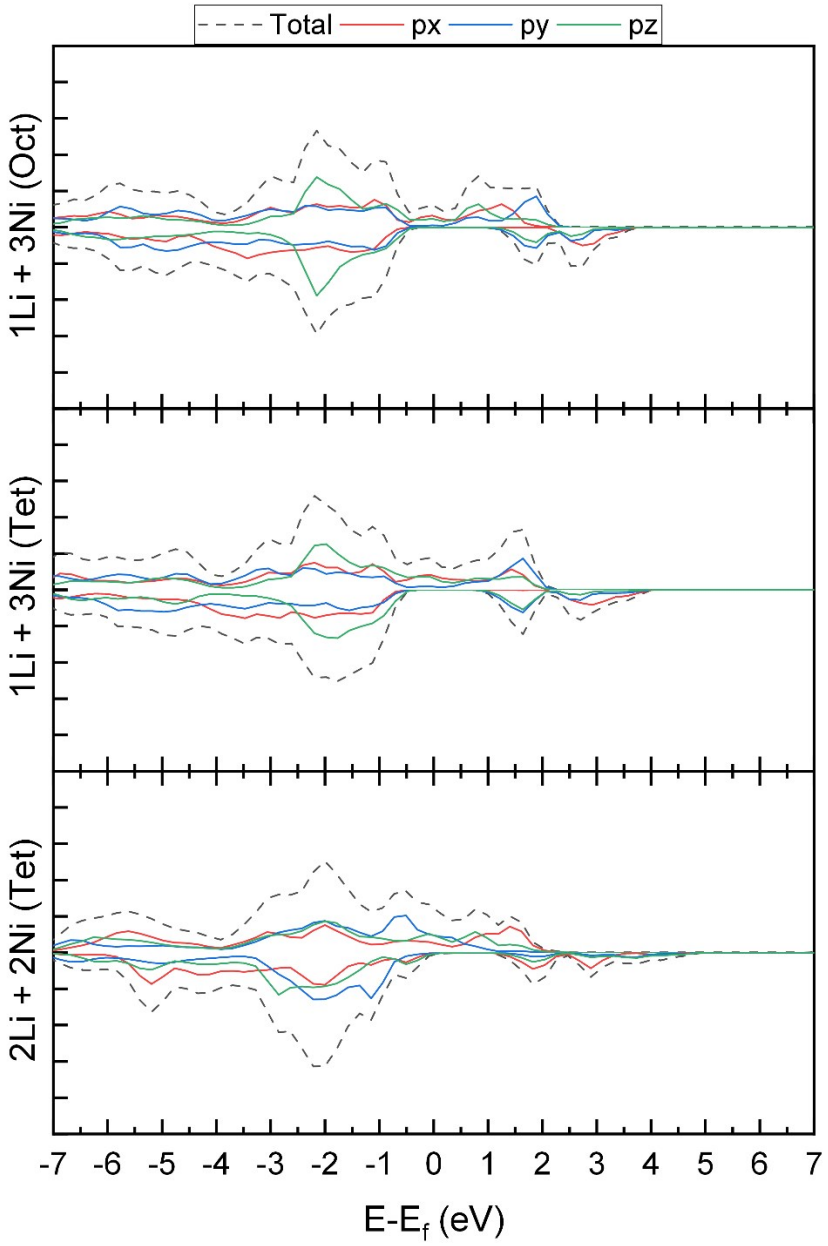

Fig. S8 Density of states for a single oxygen atom. Each of the three panels shows a different coordination configuration for an undercoordinated oxygen ion in $LiNiO_2$. The center panel shows the intermediate diffusion state in the layered phase, whereas right panel shows analogous state in the ordered phase.

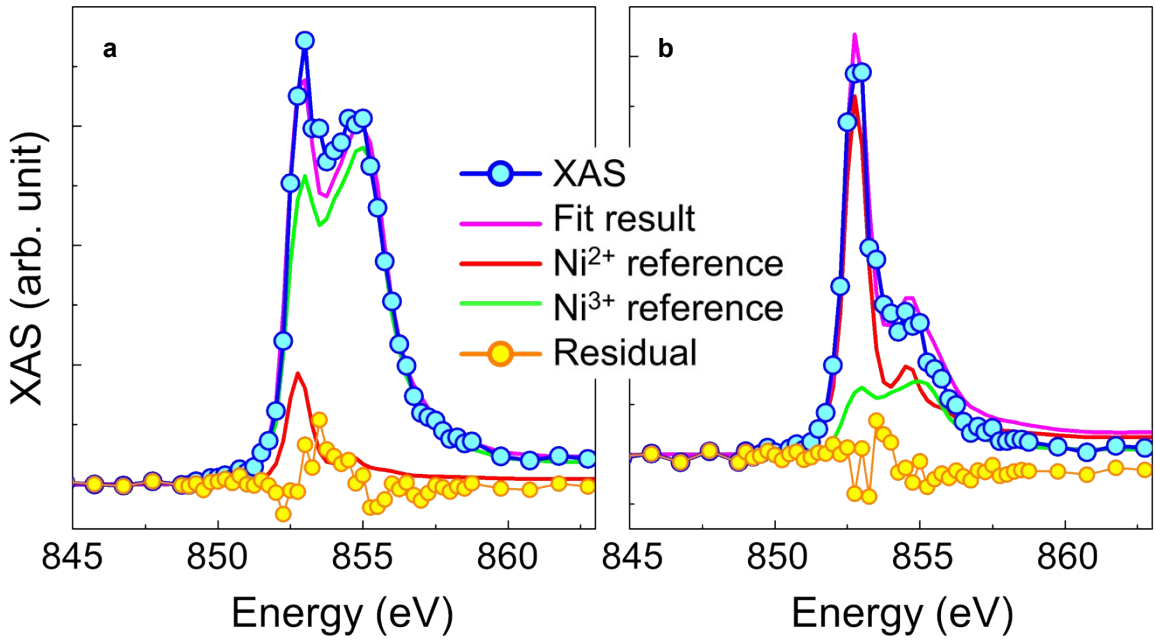

Fig. S9 Representative single-pixel XAS spectra from FIB sliced F1-GC80 after 2,000 cycles, and results of linear combination fits with standard spectra. The residual is defined by the difference between XAS data and fit results. The simulated concentrations of Ni^{2+} for pixel (a) and (b) are 19.3 % and 78.1 %, respectively.

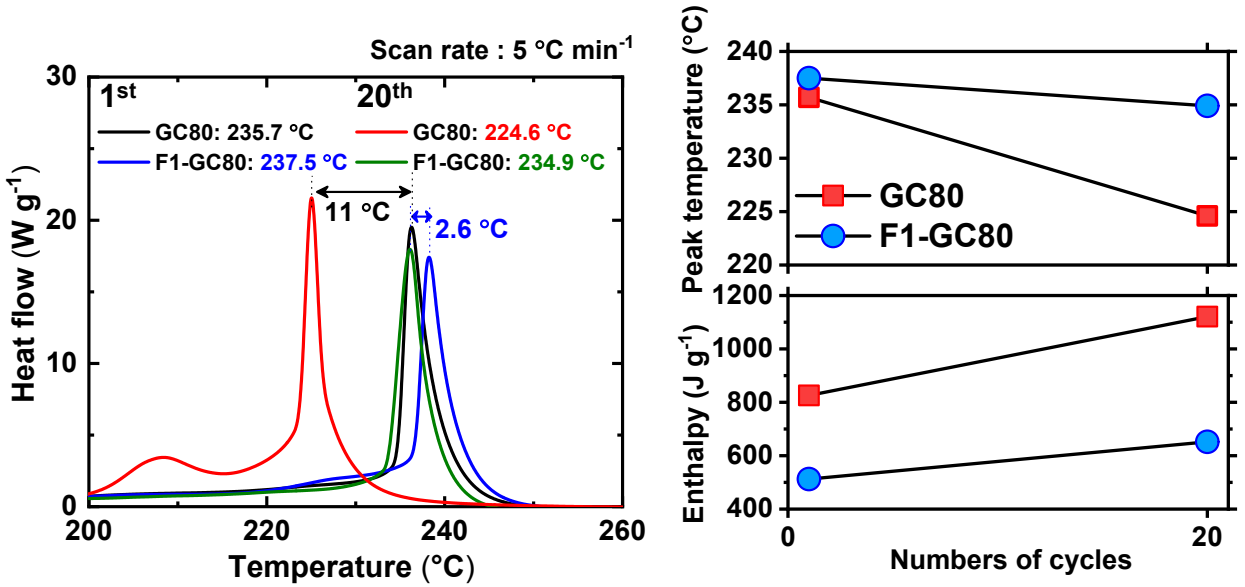

Fig. S10 DSC profiles for GC80 and F1-GC80 cathodes after the 1st and 20th cycles at 4.3 V. For F1-CG80, cation ordering was induced by F doping, which enhanced the thermal property due to the decreasing reaction with electrolyte.

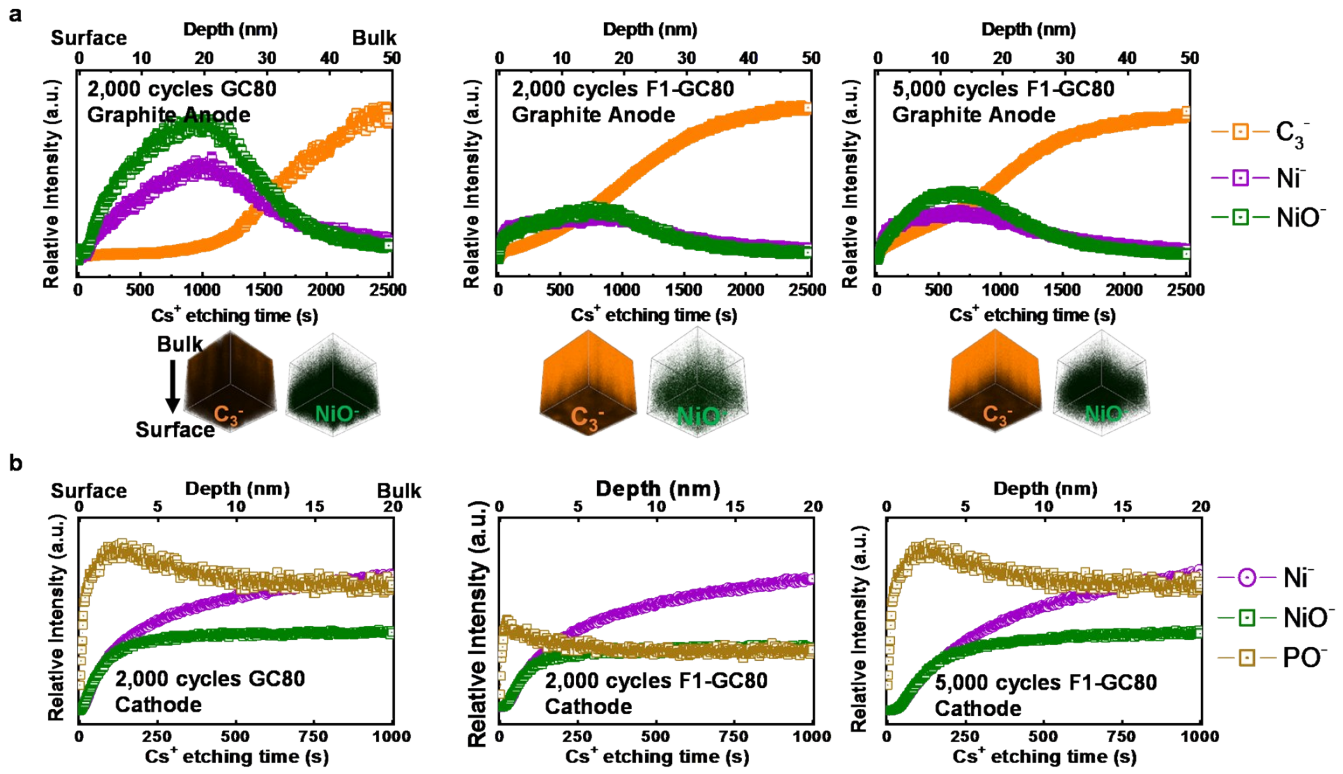

Fig. S11 Depth profiling and 3D mapping image of the (a) SEI layer on graphite anodes and (b) cathode electrolyte interphase (CEI) layer on the cathodes after 2,000 cycles for GC80 and F1-GC80 and after 5,000 cycles for F1-GC80. TOF-SIMS chemical maps of C_3^-, Ni^-, NiO^-, and PO^- as a function of depth sputtering time employed negative mode. In the SEI layer, the saturated intensity of C_3^- was used to represent graphite. In CEI layer PO- fragment was used to represent the degradation from the electrolyte.

Table S1. Chemical average composition of the cathode determined using inductively coupled plasma (ICP) analysis.

ICP (at %)	Ni	Co	Mn
GC80	**80.1**	**5.2**	**14.7**

Table S2. Structural parameters determined by Rietveld refinement of the X-ray diffraction data of z mol% F doped GC80, $Li[Ni_xCo_yMn_{1-x-y}]O_{2-z}F_z$ powder.

	a_{hex} (Å)	c_{hex} (Å)	V (Å^3)	$^a z_{ox}$	$^b S_{(TMO2)}$ (Å)	$^c I_{(LiO2)}$ (Å)	Ni^{2+} in Li layer (%)	R_p	R_{wp}	χ^2
GC80	2.87469 (5)	14.21533 (2)	101.735 (3)	0.24160 (5)	2.1304	2.6080	4.3	1.20	1.70	1.53
F1-GC80	2.87552 (4)	14.21813 (2)	101.813 (3)	0.24223 (5)	2.1487	2.5906	4.7	1.3	1.74	1.81
F2-GC80	2.87585 (5)	14.21965 (2)	101.848 (3)	0.24247 (5)	2.1558	2.5841	4.8	1.31	1.74	1.84
F10-GC80	2.87861 (5)	14.2251 (2)	102.083 (2)	0.24301 (5)	2.1720	2.5697	6.8	1.28	1.71	1.74

[a] Z_{ox} : atomic coordinate for oxygen ions

[b] Slab thickness: $S(TMO_2) = 2[(1/3) - z_{ox}]c_{hex}$

[c] Interslab space thickness: $I(LiO_2) = (c_{hex}/3) – S(TMO_2)$

Table S3. Material formation energies, O vacancy energies, and Li vacancy formation energies are listed for F-doped and pristine structures in both the layered and ordered phases. Different stoichiometries were necessary to represent the completely delithiated states – NiO_2 for the layered phase and NiO for the ordered phase.

Structure	F doping (%)	Energy per formula unit		
		$LiNiO_2$	$Li_{0.5}NiO_2$	NiO_2 (layered) NiO (ordered)
Layered	0 (Pristine)	-3.968	-2.048	-0.146
	4	-4.125	-2.274	-0.179
Ordered	0 (Pristine)	-3.932	-2.307	-0.295
	4	-4.069	-2.440	-0.227