

## Manipulating the crystal plane angle within primary particle arrangement for the radial ordered structure in Ni-rich cathode

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### 1. Experimental section

#### 1.1 Preparation of Ni-rich cathode

For the doped nickel-rich cathode,  $\text{Ni}_{0.86}\text{Co}_{0.08}\text{Mn}_{0.06}(\text{OH})_2$  precursor, oxides  
( $\text{TMO}_2 = \text{WO}_3, \text{B}_2\text{O}_3$ ), and  $\text{LiOH}\cdot\text{H}_2\text{O}$  are weighed and evenly mixed according to the  
molar ratio of 0.99:0.01:1.02, and the evenly mixed sample was placed in a tubular

furnace with oxygen atmosphere at 480 °C for 5 h and then cooled to room temperature. Subsequently, the presintered products were pressed into disks and calcined at 750 °C for 20 h followed by quenching to room temperature.

## **1.2 Material characterization**

The composition of different nickel-rich cathode materials (including doped and undoped) was determined by ICP-OES (OPTIMA 4300 DV, PerkinElmer). Scanning electron microscope and focused ion beam (FIB, FEI) were used to analyze the surface particles and profile structure of nickel-rich cathode (SEM, FEI Nova Nano SEM 460). X-ray powder diffraction (Bruker D8 Advance and Cu  $K\alpha$  ( $\lambda= 1.5418 \text{ \AA}$ )) characterizes the crystal structure and lattice parameters. STEM was employed for detailed spectroscopic analysis, and Pt is added at the top of the sample as a protective layer to protect particles from damage. All the STEM images using a HAADF detector.

## **1.3 Electrochemical measurement**

The cathode is prepared by mixing the active material, Super P and polyvinylidene fluoride (mass ratio 8:1:1) with a certain amount of N-methyl-2-pyrrolidone (NMP) into the slurry. The Al foil is evenly coated with the slurry and dried in a vacuum oven at 120 °C for 12 hours. The mass loading of the electrode is 4-5mg cm<sup>-2</sup>, and it is assembled into a button battery. The glove box requires that the water and oxygen content be less than 0.1ppm. Electrolyte (1.2 M LiPF<sub>6</sub> dissolved in a solution of FEC/FEMC/HFE) was used. Electrochemical test equipment is Neware battery test system (CT-4008T-5V20mA-164, Shenzhen, China). The batteries were tested in the voltage windows of 3.0-4.6 V at room temperature (25 °C).

## **1.4 Computation details**

All the density functional theory calculations were performed by using the Vienna ab initio Simulation Program (VASP). [1,2] The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form and a cutoff energy of 500 eV for planewave basis set were adopted.[3] The 10 × 10 × 1 and 1 × 10 × 1 Monkhorst-Pack grid was used for sampling the Brillouin zones at structure optimization for (003) and (104) surfaces, respectively. [4] The ion-electron interactions were described by the projector augmented wave (PAW) method.[5] The convergence criteria of structure

optimization were choose as the maximum force on each atom less than  $0.01 \text{ eV}/\text{\AA}$  with an energy change less than  $1 \times 10^{-5} \text{ eV}$ . The Surface energy ( $E_{\text{sur}}$ ) for each elemental step is defined as:

$$\Delta E_{\text{surf}} = \Delta E_{\text{cleave}} + \Delta E_{\text{relax}} = \frac{1}{2}(E_{\text{cleaved}} - E_{\text{bulk}}) + (E_{\text{relaxed}} - E_{\text{cleaved}}) \quad (1)$$

where  $\Delta E_{\text{cleave}}$  is the cleaving energy which arises due to bond breaking between atoms to create two new surfaces on either side of the vacuum slab.  $\Delta E_{\text{cleave}}$  was calculated by subtracting the energy of the original bulk crystal ( $E_{\text{bulk}}$ ) from that of the as-cleaved crystal ( $E_{\text{cleaved}}$ , without relaxation of the surface atoms).

## 2. Supporting Figures and text

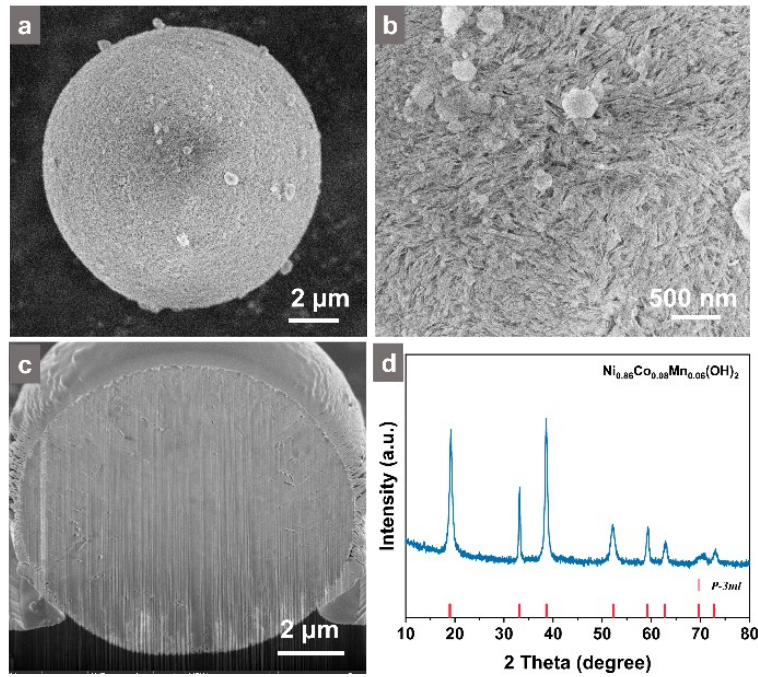


Fig. S1 (a) SEM image and (b) local enlarged image of  $\text{Ni}_{0.86}\text{Co}_{0.08}\text{Mn}_{0.06}(\text{OH})_2$ , and (c) cross-sectional image and (d) XRD spectra of  $\text{Ni}_{0.86}\text{Co}_{0.08}\text{Mn}_{0.06}(\text{OH})_2$ .

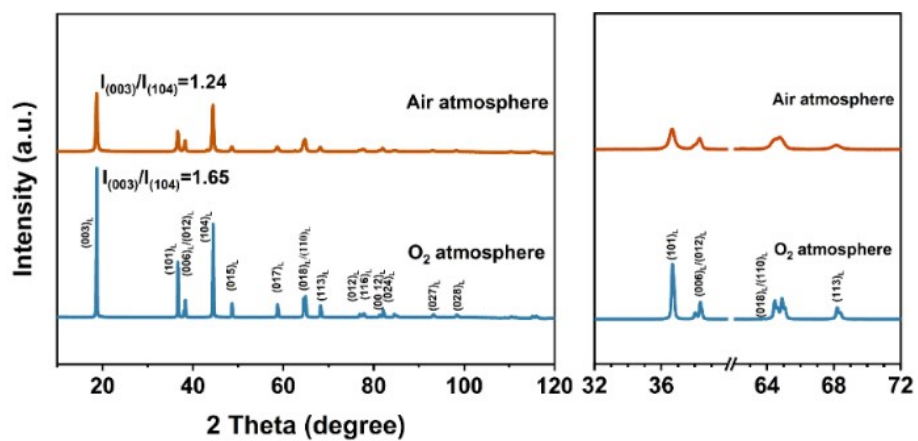


Fig. S2 XRD spectra of Ni-rich cathode materials prepared in air and oxygen atmosphere.

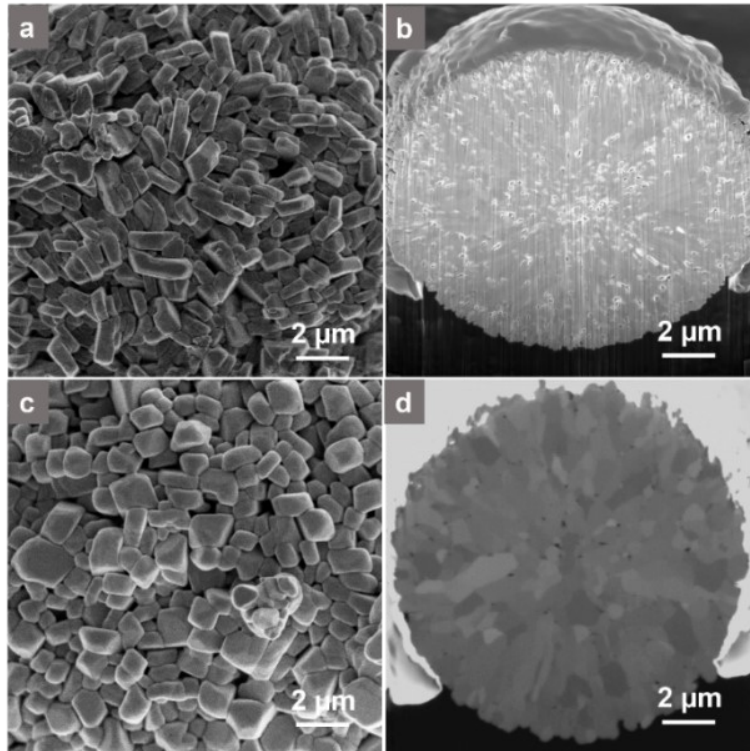


Fig. S3 SEM images of surface particles and cross section of Ni-rich cathode prepared in (a-b) air atmosphere and (c-d) oxygen atmosphere.

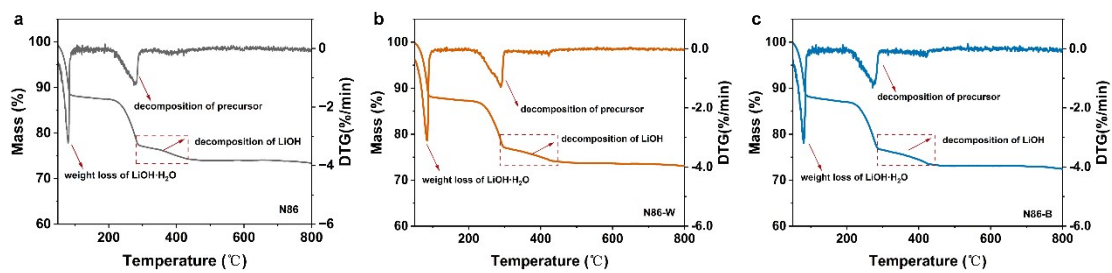


Fig. S4 TG spectra of (a) N86, (b) N86-W, and (c) N86-B mixture systems.

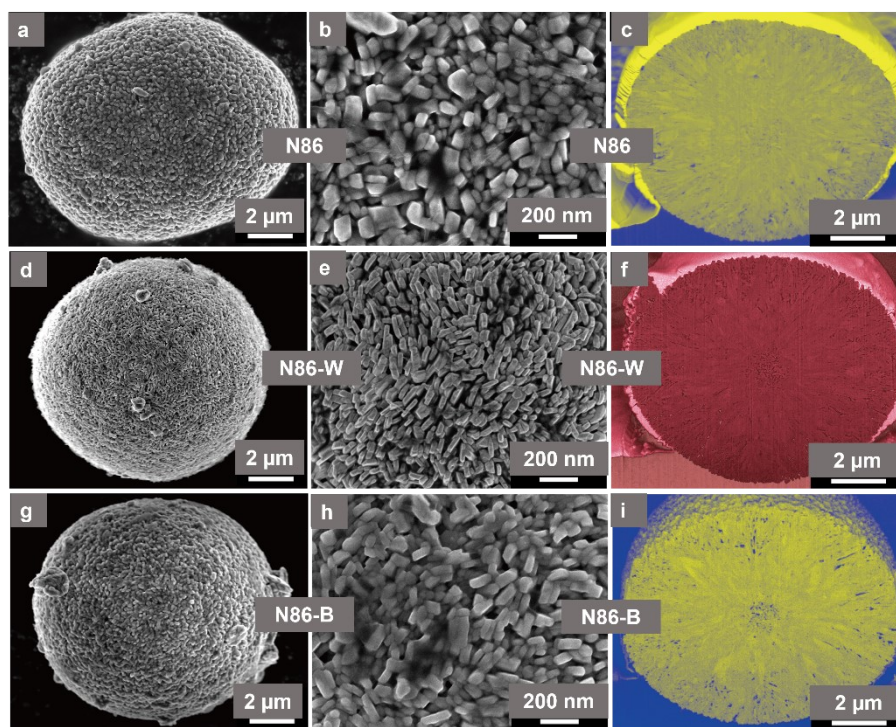


Fig. S5 SEM images of surface morphology and cross-sectional section of (a-c) N86, (d-f) N86-W, and (g-i) N86-B samples quenched at 750 °C

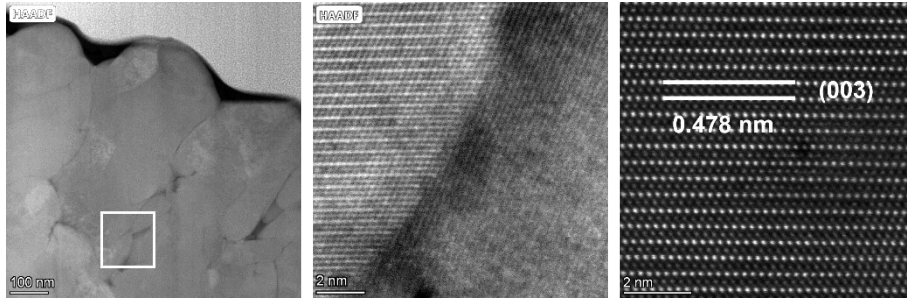


Fig. S6. Magnified STEM image of primary particles from N86-W.



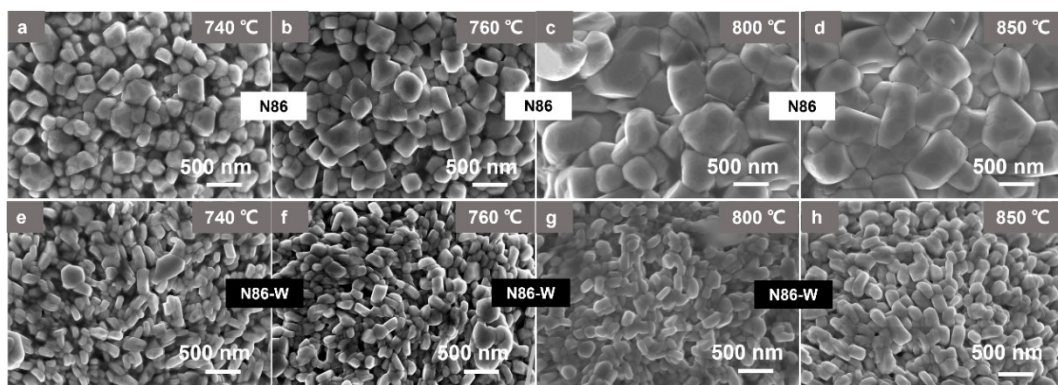


Fig. S7 SEM images of (a-d) N86 and (e-h) N86-W prepared at 740, 760, 800 and 850 °C.

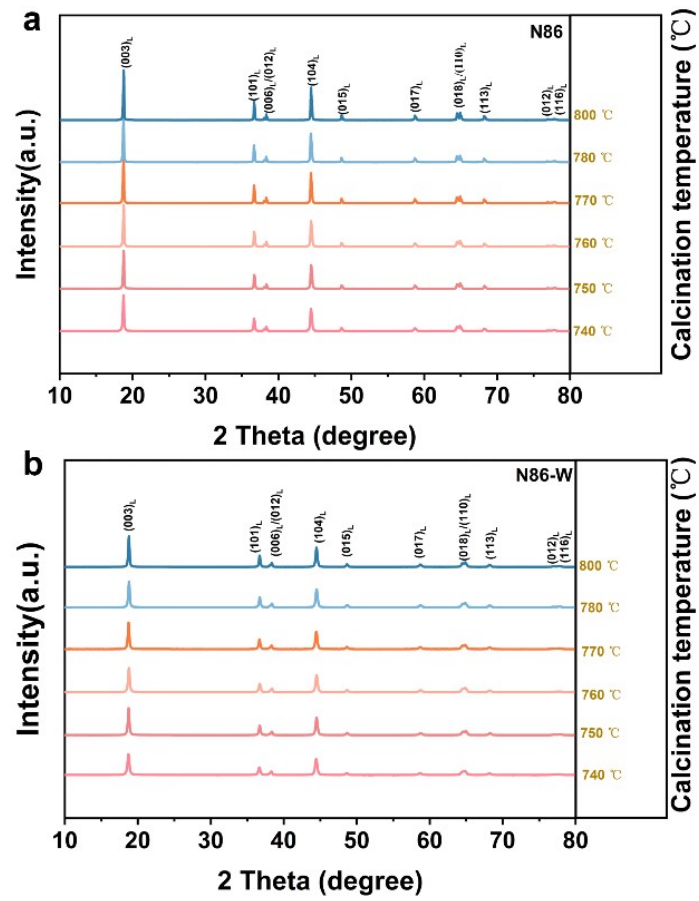


Fig. S8 XRD patterns of (a) N86 and (b) N86-W prepared at 740, 750, 760, 770, 780, and 800 °C.

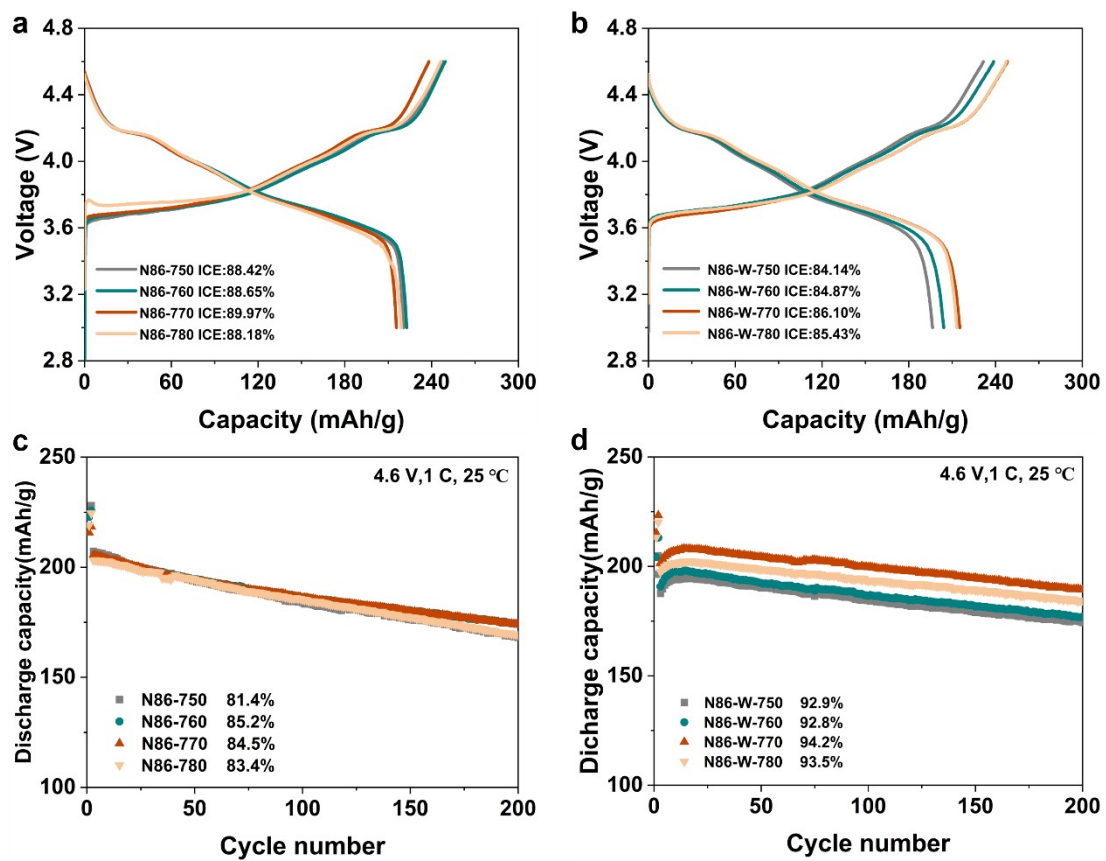


Fig. S9 (a-b) First charge-discharge curves and (c-d) cyclic performance of N86 and N86-W electrodes prepared at 750-780 °C.

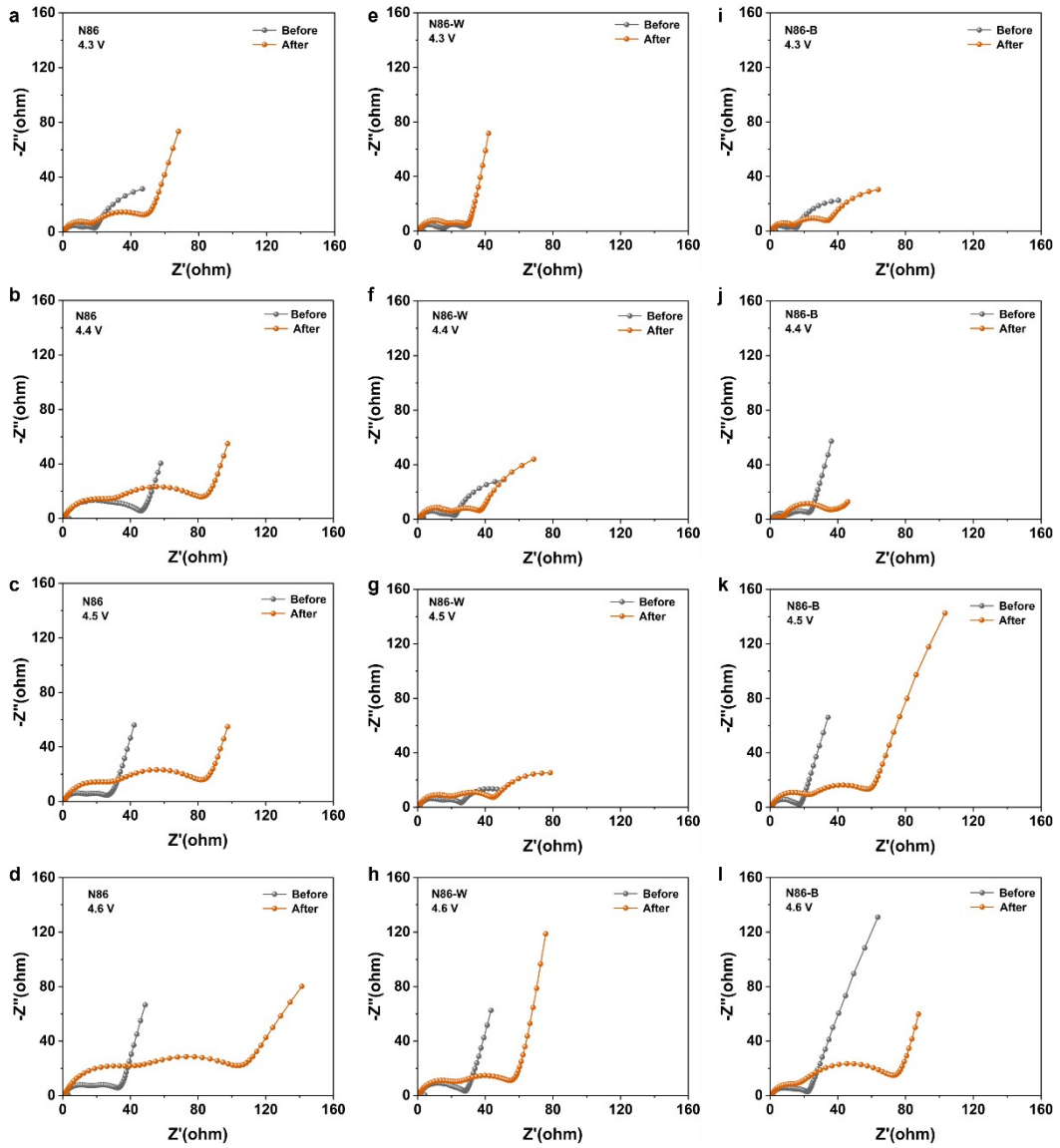


Fig. S10 EIS results of (a-d) N86, (e-h) N86-W, and (i-l) N86-B before and after being charged to different potentials and then stored at 60 °C for 5 days.

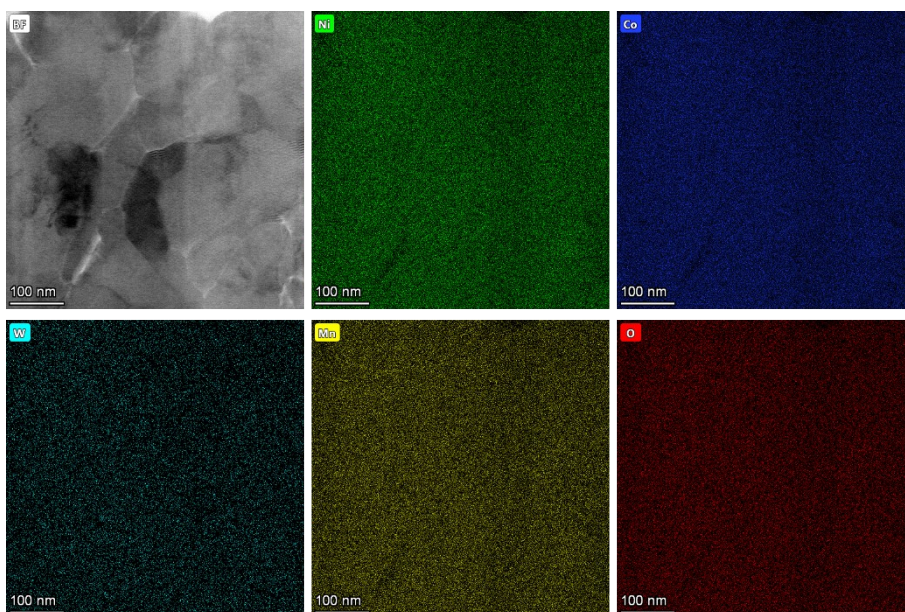


Fig. S11 Bright-field (BF) STEM image and EDS elemental maps of Ni, Co, Mn, W and O.

Table S1. Cell parameters and  $I_{(003)}/I_{(104)}$  value of cathode materials after XRD refinement

Sample	<i>a</i>	<i>c</i>	<i>c/a</i>	$I_{(003)}/I_{(104)}$
N86	2.8725	14.1923	4.9407	1.65
N86-B	2.8741	14.2012	4.9470	1.66
N86-W	2.8737	14.2117	4.9454	1.62

Table S2.  $I_{(003)}/I_{(104)}$  value of N86 and N86-W prepared at 740, 750, 760, 770, 780 and 800 °C

Sample	$I_{(003)}/I_{(104)}$					
	740 °C	750 °C	760 °C	770 °C	780 °C	800 °C
N86	1.6271	1.6559	1.6773	1.6496	1.5888	1.5400
N86-W	1.3086	1.3470	1.5423	1.6155	1.6082	1.4708

### Supplementary References

- [1] G.Kresse, J. Furthmüller, Comput. Mater. Sci. 1 (1996) 15-50.
- [2] G.Kresse, J. Furthmüller, Phys. Rev. B. 16 (1996) 11169-11186.
- [3] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 18 (1996) 3865-3868.
- [4] H.J. Monkhorst, J.D. Pack, Phys. Rev. B. 13 (12) (1976) 5188-5192.
- [5] P.E. Blöchl, Phys. Rev. B. 50 (24) (1994) 17953-17979.