Advancing layered cathode material's cycling stability from uniform doping to non-uniform doping

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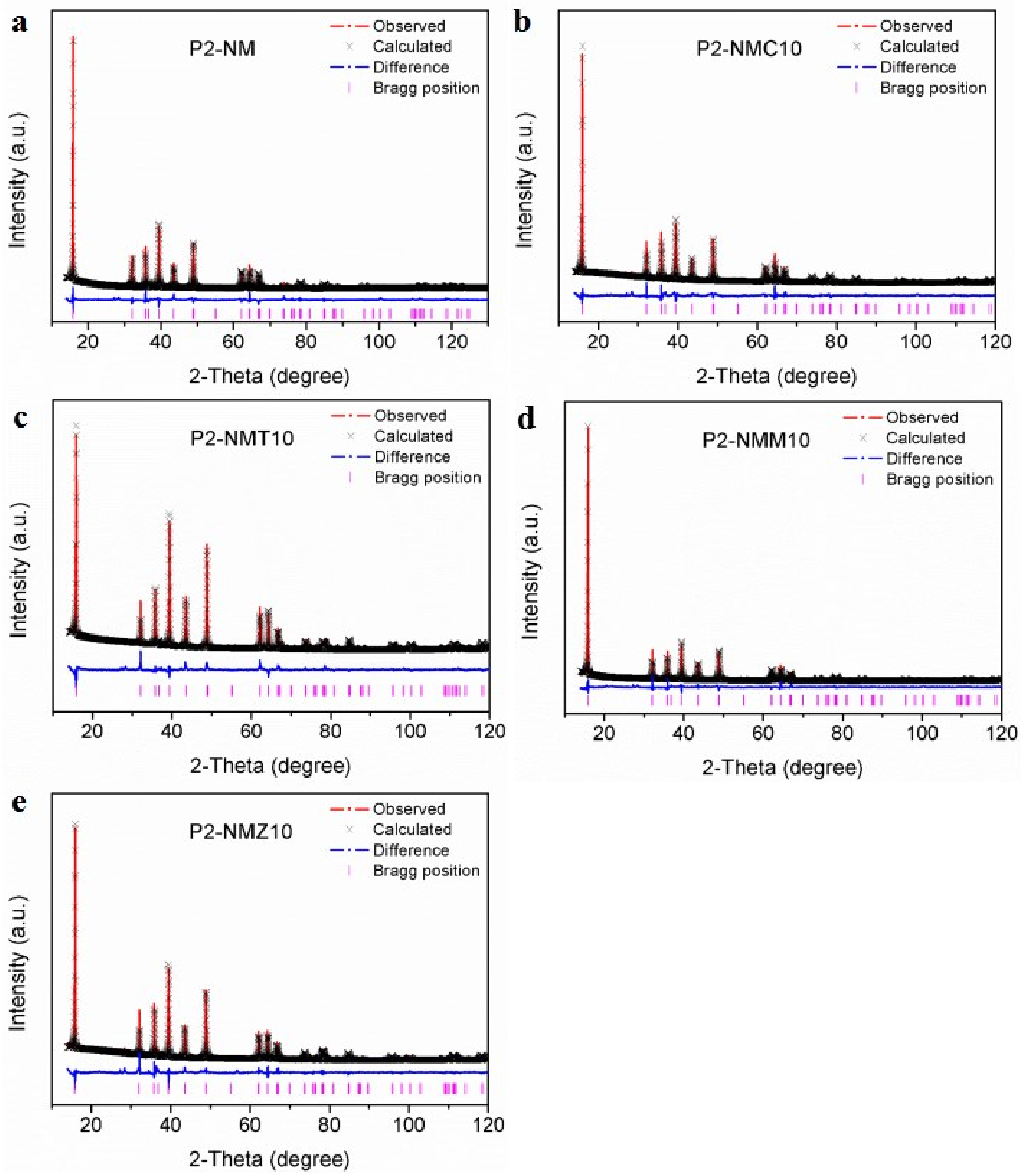

Figure S1. XRD Rietveld refinement patterns of (**a**) P2-$Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$ (P2-NM), (**b**) P2-$Na_{0.67}Ni_{0.23}Mn_{0.67}Cu_{0.1}O_2$ (P2-NMC10), (**c**) P2-$Na_{0.67}Ni_{0.33}Mn_{0.57}Ti_{0.1}O_2$ (P2-NMT10), (**d**) P2-$Na_{0.67}Ni_{0.23}Mn_{0.67}Mg_{0.1}O_2$ (P2-NMM10), (**e**) P2-$Na_{0.67}Ni_{0.23}Mn_{0.67}Zn_{0.1}O_2$ (P2-NMZ10), which confirm that the materials are all in P2 layered structure with the $P6_3/mmc$ space group.

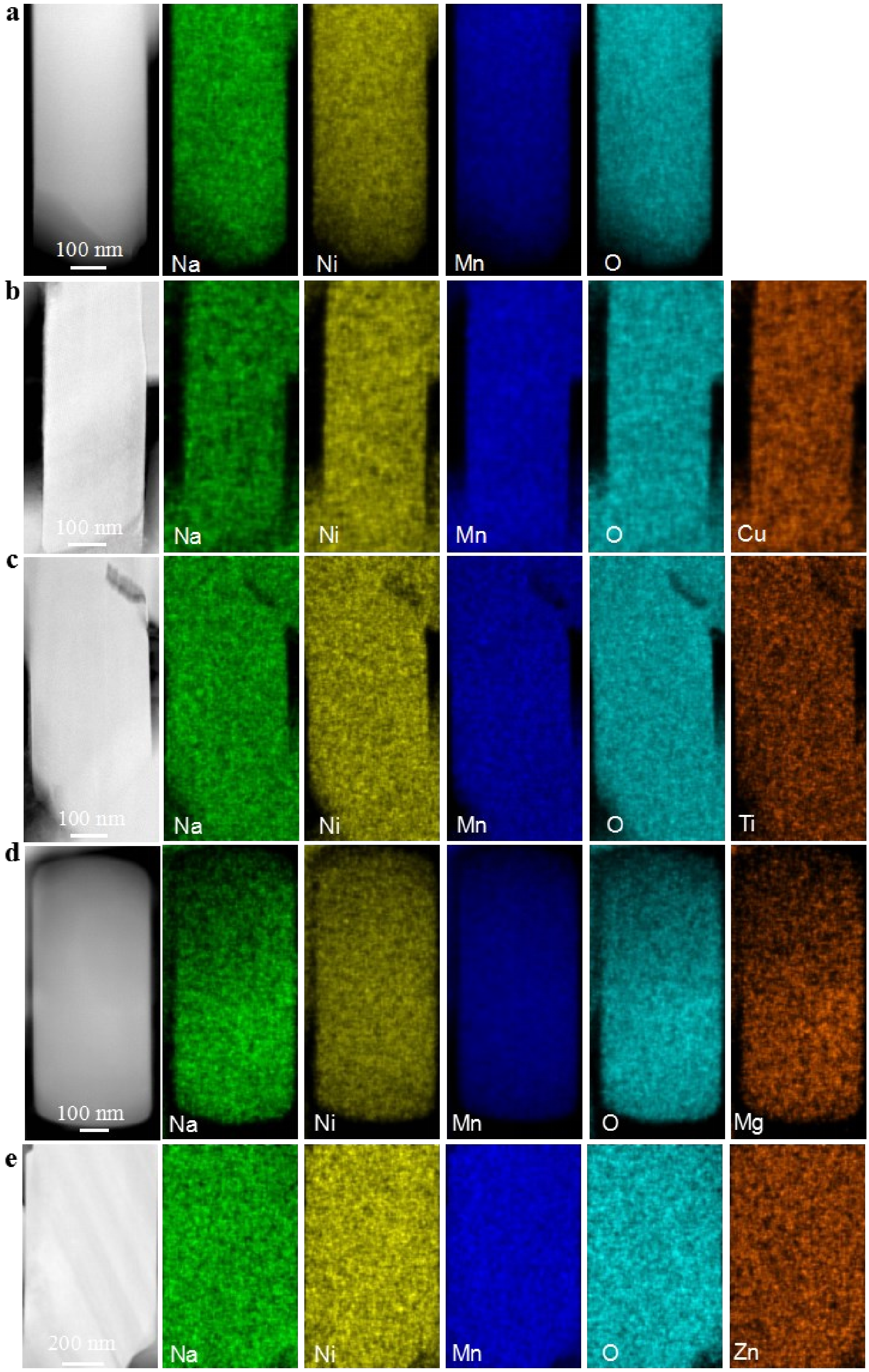

Figure S2. STEM-EDS mappings show that elements are uniformly distributed in the as-prepared samples. (a) P2-NM, (b) P2-NMC10, (c) P2-NMT10, (d) P2-NMM10 and (e) P2-NMZ10.

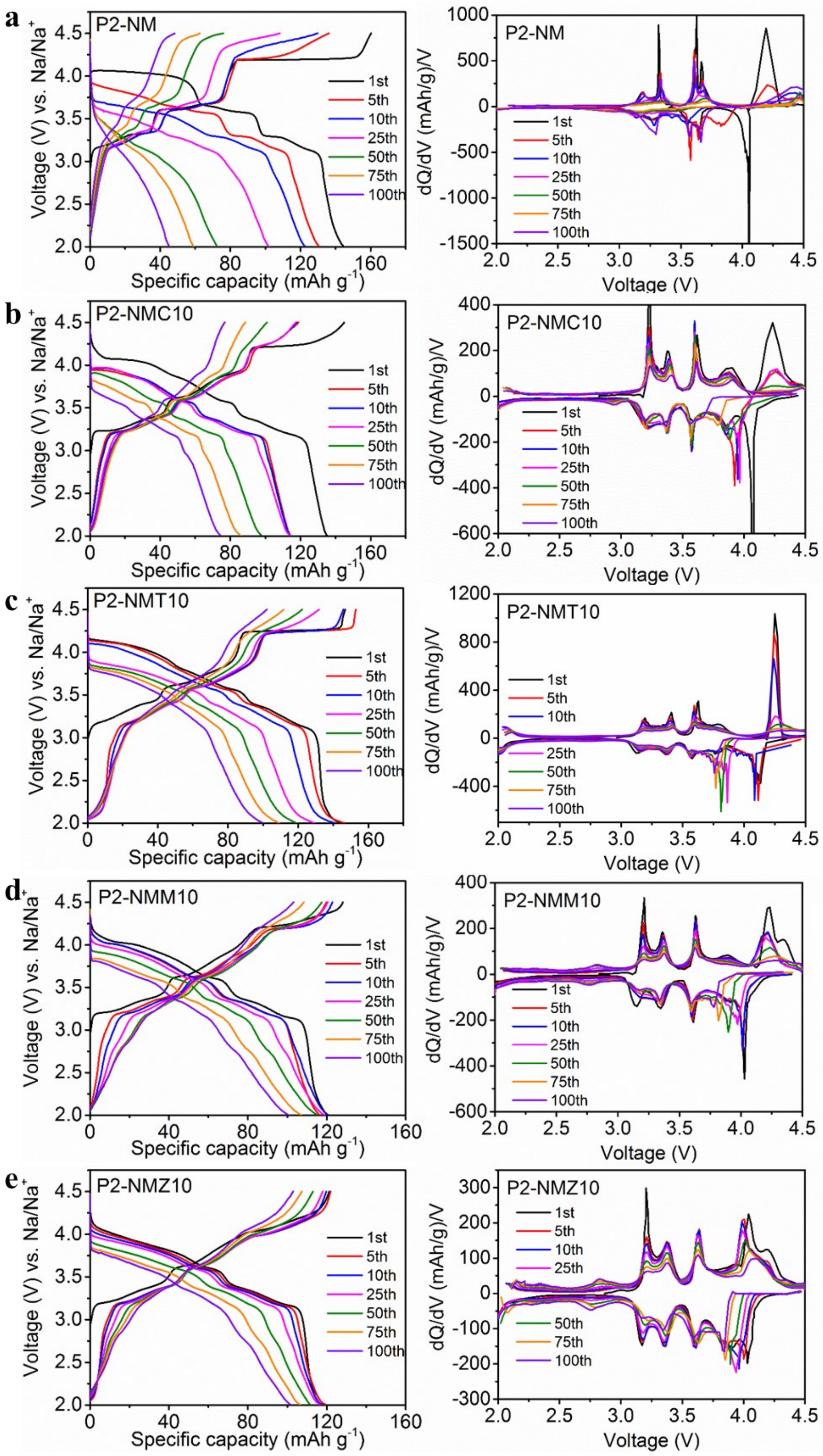

Figure S3. Charge/discharge voltage profiles and corresponding dQ/dV curves of the five cathodes cycled at 2.0-4.5 V. (**a**) P2-NM, (**b**) P2-NMC10, (**c**) P2-NMM10, (**d**) P2-NMM10 and (**e**) P2-NMZ10 .

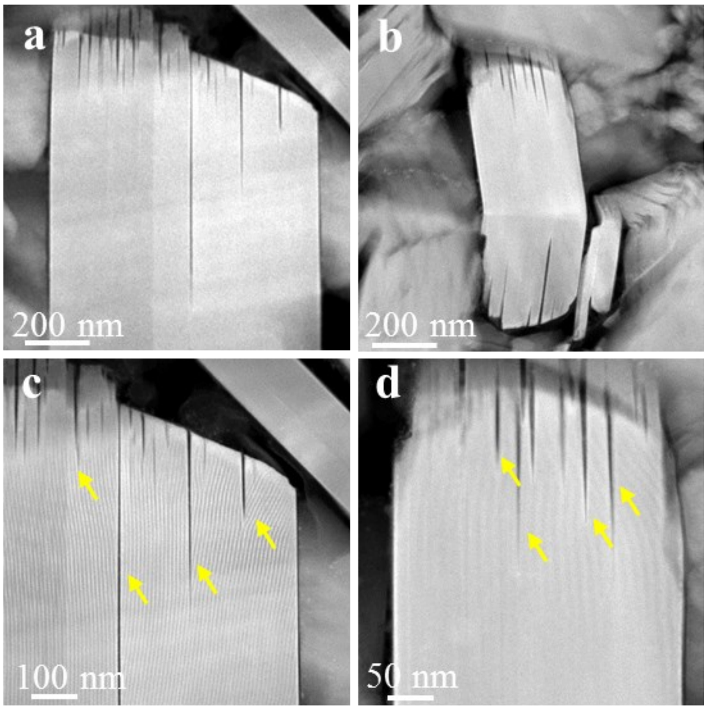

Figure S4. Low magnification cross sectional STEM-HAADF images show cracks (highlighted by yellow arrows) in the P2-NMC10 cathode after 50 cycles.

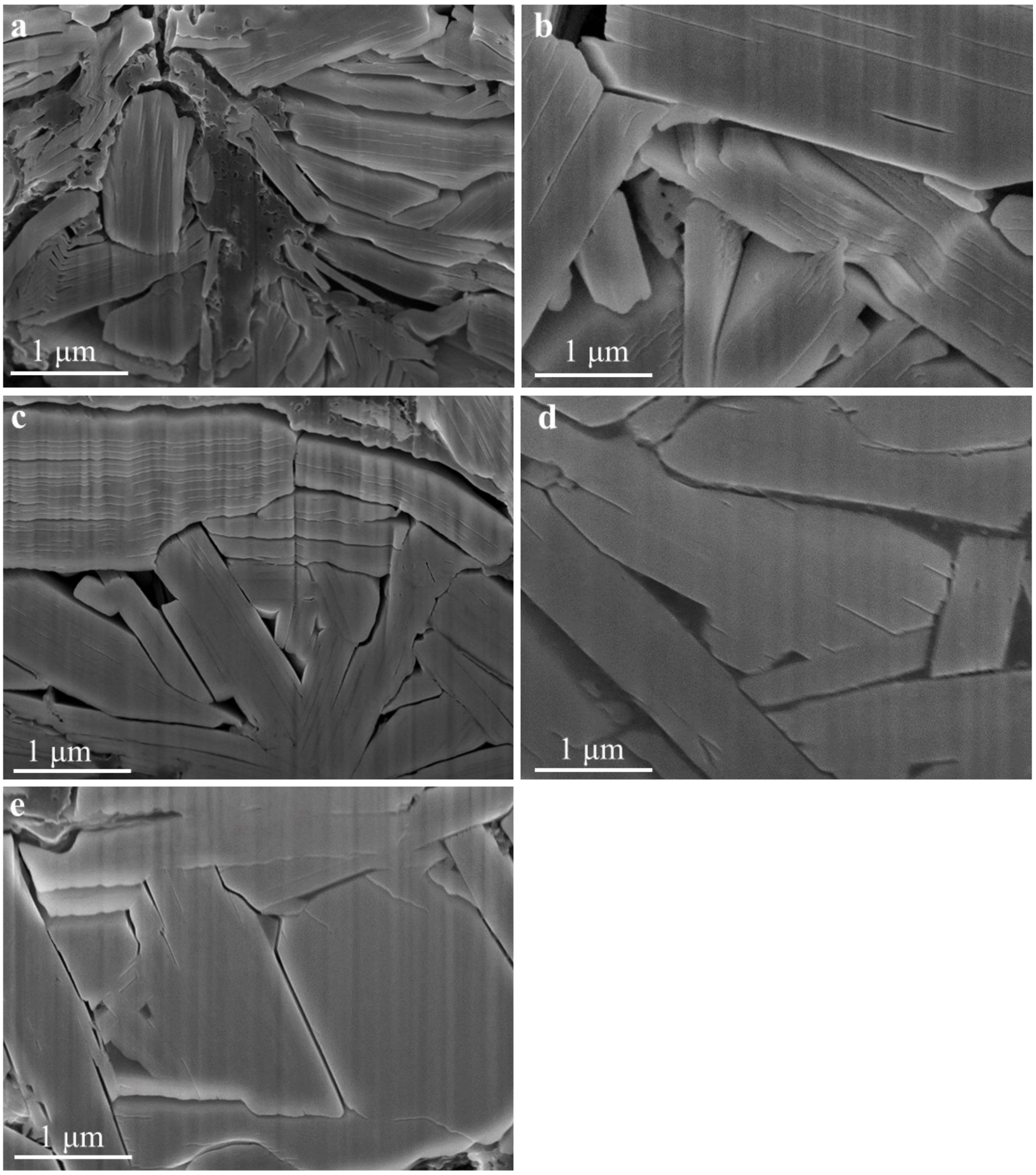

Figure S5. Cross sectional SEM images for the different cathode samples after 50 cycles at 2.0-4.5 V. (**a**) P2-NM sample. (**b**) P2-NMC10 sample. (**c**) P2-NMT10 sample. (**d**) P2-NMM10 sample. (**e**) P2-NMZ10 sample.

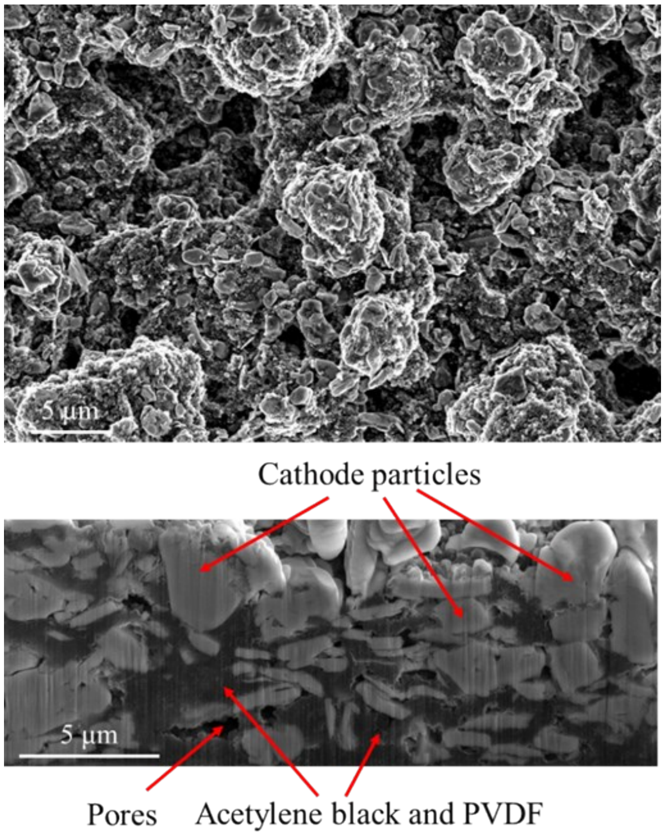

Figure S6. (a) The plan-view and (b) cross-sectional SEM image of the P2-NMZ10 cathode materials showing the distribution of pores, cathode particles, acetylene black and PVDF.

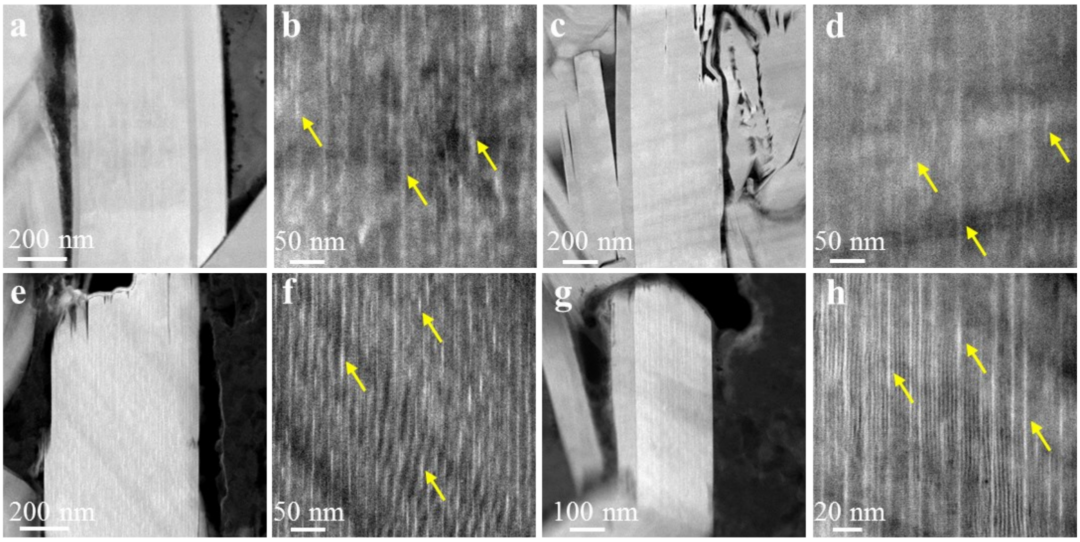

Figure S7. Observing bright stripes (highlighted by yellow arrows) in (**a-d**) P2-NMM10 and (**e-h**) P2-NMZ10 after 50 cycles at 2.0-4.5 V by STEM-HAADF.

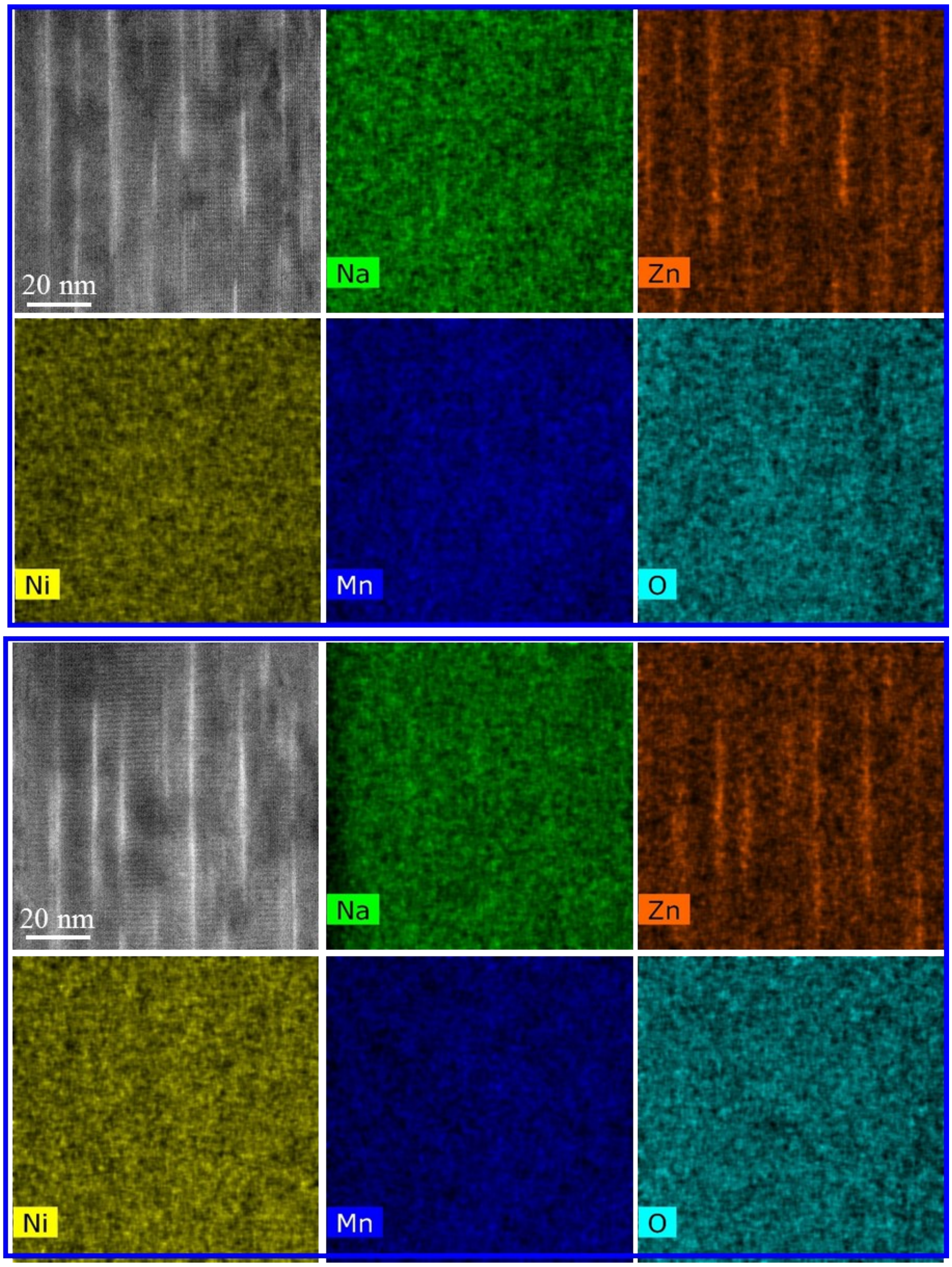

Figure S8. STEM-HAADF images and corresponding EDS of P2-NMZ10 after 50 cycles at 2.0-4.5 V, showing that only Zn element segregation in bright stripes.

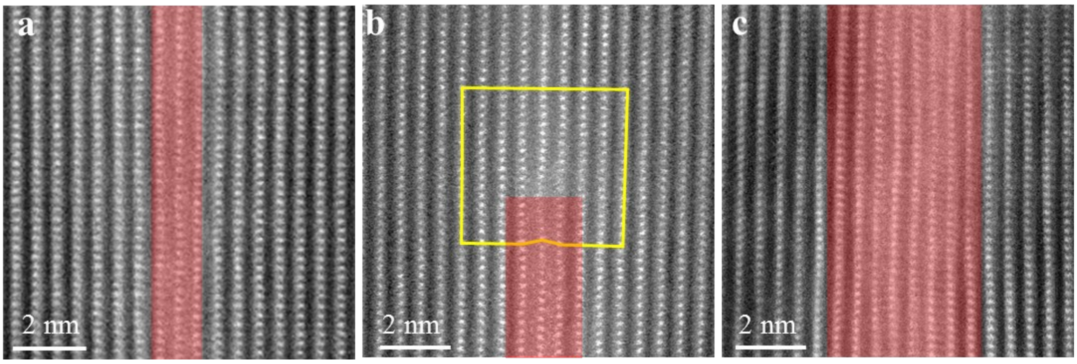

Figure S9, a, A two-layer thick precipitate. **b**, A multi-layer thick precipitate with one end terminated in the P2 structured matrix. The yellow circuit highlights a zigzag stacking sequence due to displacement. **c**, A multi-layer thick precipitate. The red regions highlight the lattice structure change.

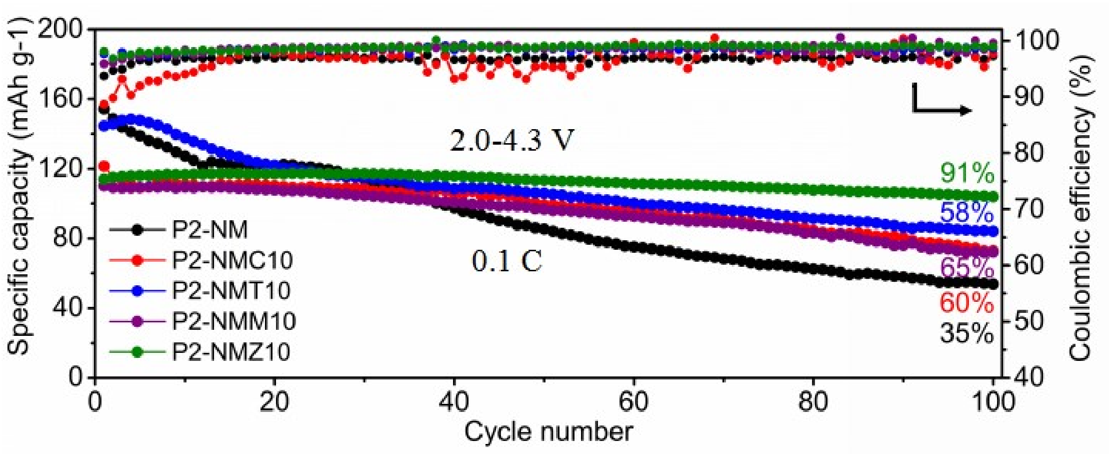

Figure S10. Electrochemical performance of the five P2-structured cathode materials (P2-NM, P2-NMC10, P2-NMT10, P2-NMM10 and P2-NMZ10) cycled at 2.0-4.3 V after 100 cycles.

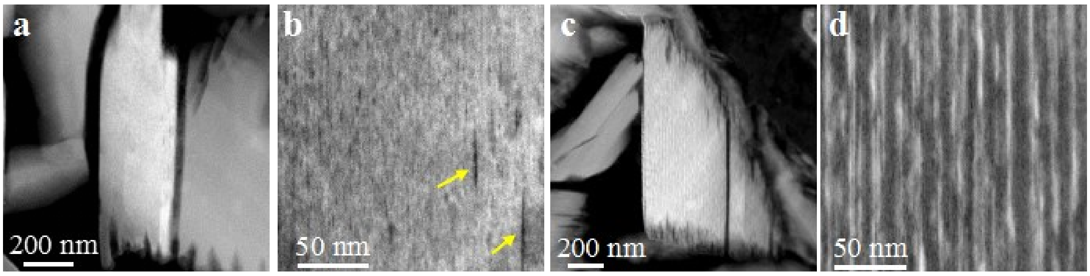

Figure S11. Cross sectional STEM-HAADF images of the (**a, b**) P2-NMM10and (**c, d**) P2-NMZ10 cathodes cycled at 4.5 V after 200 cycles, respectively. **b**, no bright stripes, high density of dark spots and low density of cracks in P2-NMM10 cathode. Yellow arrows in (**b**) highlight the cracks in grain interior induced by high density of dark spots. **d**, high density of bright stripes, low density of dark spots and no cracks in P2-NMZ10 cathode.

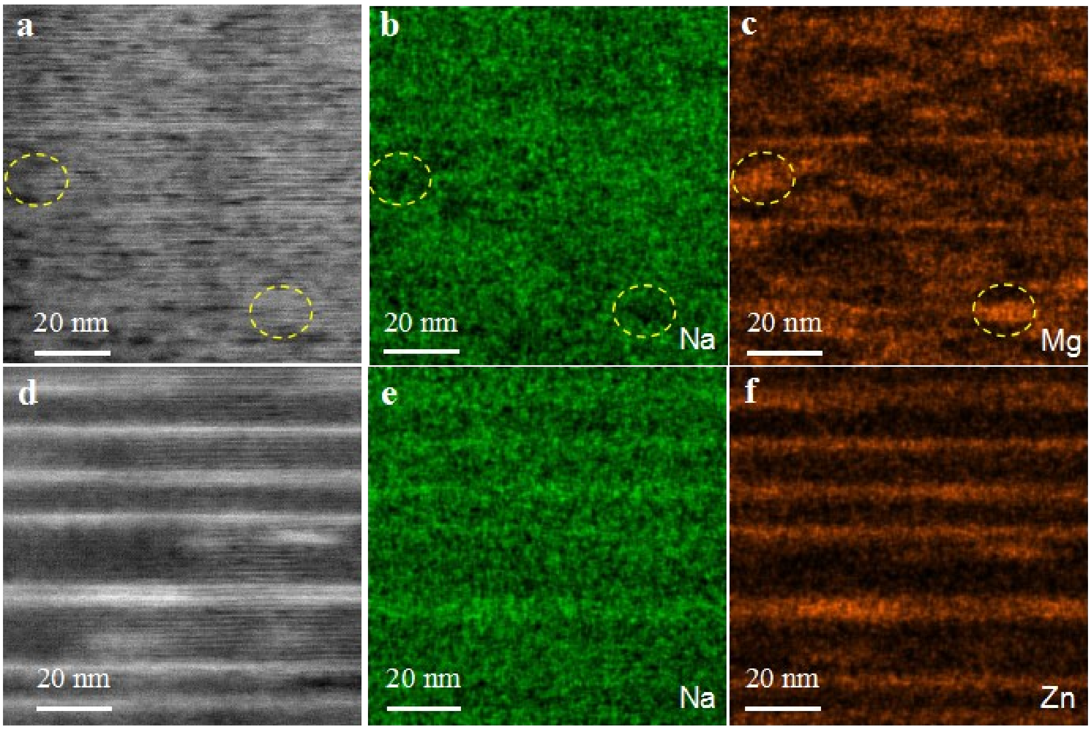

Figure S12. Cross sectional STEM-HAADF images of the (**a-c**) P2-NMM10 and (**d-f**) P2-NMZ10 cathodes cycled at 4.5 V after 200 cycles. **a**, Contrast from the precipitates become weaker and high density of dark spots appear in P2-NMM10 sample cycled at 4.5 V after 200 cycles. (**b**, **c**) EDS mappings show the distributions of Na and Mg are not uniform. Mg dopant segregation is evident. **d**, High density of bright stripes in P2-NMZ10 sample cycled at 4.5 V after 200 cycles. (**e**, **f**) The EDS mappings show the precipitates are Na-rich and Zn-rich regions.

Table S1. Crystallographic parameters of synthesized P2-$Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$ (P2-NM) refined by the Rietveld method

Space group	**P6$_3$/mmc**	**No.194**			
Atom	**site**	**X**	**Y**	**Z**	**Occ.**
Na$_f$	2b	0	0	0.25	0.2358
Na$_e$	2d	0.3333	0.6667	0.25	0.4000
Ni	2a	0	0	0	0.3333
Mn	2a	0	0	0	0.6667
O	4f	0.6667	0.3333	0.0875	1.0000
a=2.8933(4) Å	c=11.1561(9) Å	V=80.880(9) Å^3	Rp=2.74%	Rwp=4.04%	S=2.6090

Table S2. Crystallographic parameters of synthesized P2-$Na_{0.67}Ni_{0.23}Mn_{0.67}Cu_{0.1}O_2$ (P2-NMC10) refined by the Rietveld method.

Space group	**P6$_3$/mmc**	**No.194**			
Atom	**site**	**X**	**Y**	**Z**	**Occ.**
Na$_f$	2b	0	0	0.25	0.2139
Na$_e$	2d	0.3333	0.6667	0.25	0.4506
Ni	2a	0	0	0	0.2235
Mn	2a	0	0	0	0.6624
Cu	2a	0	0	0	0.1
O	4f	0.6667	0.3333	0.07682	1.0000
a=2.8938(9) Å	c=11.1675(1) Å	V=80.993(7) Å^3	Rp=2.782%	Rwp=4.05%	S=2.6380

Table S3. Crystallographic parameters of synthesized P2-$Na_{0.67}Ni_{0.33}Mn_{0.57}Ti_{0.1}O_2$ (P2-NMT10) refined by the Rietveld method.

Space group	**P6$_3$/mmc**	**No.194**			
Atom	**site**	**X**	**Y**	**Z**	**Occ.**
Na$_f$	2b	0	0	0.25	0.2157
Na$_e$	2d	0.3333	0.6667	0.25	0.4521
Ni	2a	0	0	0	0.3222
Mn	2a	0	0	0	0.5597
Ti	2a	0	0	0	0.1
O	4f	0.6667	0.3333	0.07992	1.0000
a=2.9002(5) Å	c=11.1210(0) Å	V=81.229(9) Å^3	Rp=2.069%	Rwp=3.33%	S=2.1560

Table S4. Crystallographic parameters of synthesized P2-$Na_{0.67}Ni_{0.23}Mn_{0.67}Mg_{0.1}O_2$ (P2-NMM10) refined by the Rietveld method.

Space group	**$P6_3/mmc$**	**No.194**			
Atom	**site**	**X**	**Y**	**Z**	**Occ.**
Na_f	2b	0	0	0.25	0.2139
Na_e	2d	0.3333	0.6667	0.25	0.4561
Ni	2a	0	0	0	0.2316
Mn	2a	0	0	0	0.6684
Mg	2a	0	0	0	0.1
O	4f	0.6667	0.3333	0.07992	1.0000
a=2.8943(9) Å	c=11.1708(6) Å	V=81.046(2) Å^3	Rp=3.256%	Rwp=4.77%	S=2.4339

Table S5. Crystallographic parameters of synthesized P2-$Na_{0.67}Ni_{0.23}Mn_{0.67}Zn_{0.1}O_2$ (P2-NMZ10) refined by the Rietveld method.

Space group	**$P6_3/mmc$**	**No.194**			
Atom	**site**	**X**	**Y**	**Z**	**Occ.**
Na_f	2b	0	0	0.25	0.2169
Na_e	2d	0.3333	0.6667	0.25	0.4516
Ni	2a	0	0	0	0.2214
Mn	2a	0	0	0	0.6632
Zn	2a	0	0	0	0.1
O	4f	0.6667	0.3333	0.09089	1.0000
a=2.8987(9) Å	c=11.1750(9) Å	V=81.323(4) Å^3	Rp=2.934%	Rwp=4.403%	S=2.6382