ADVANCED MATERIALS

Supporting Information

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Dopant Segregation Boosting High-Voltage Cyclability of Layered Cathode for Sodium Ion Batteries

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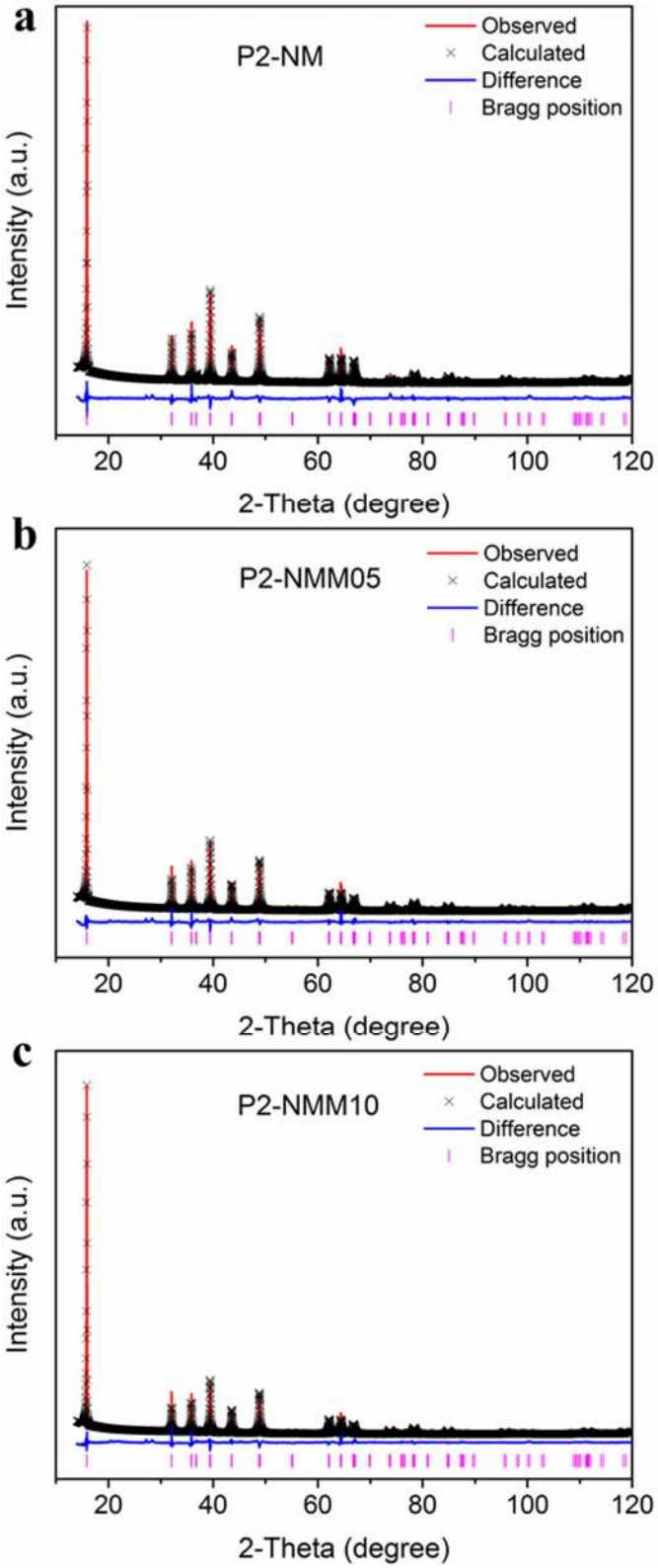

Figure S1. XRD and corresponding Rietveld refinement results of (**a**) P2-NM, (**b**) P2-NMM05 and (**c**) P2-NMM10, which confirm that all the three samples are in P2 layered structure with the $P6_3/mmc$ space group.

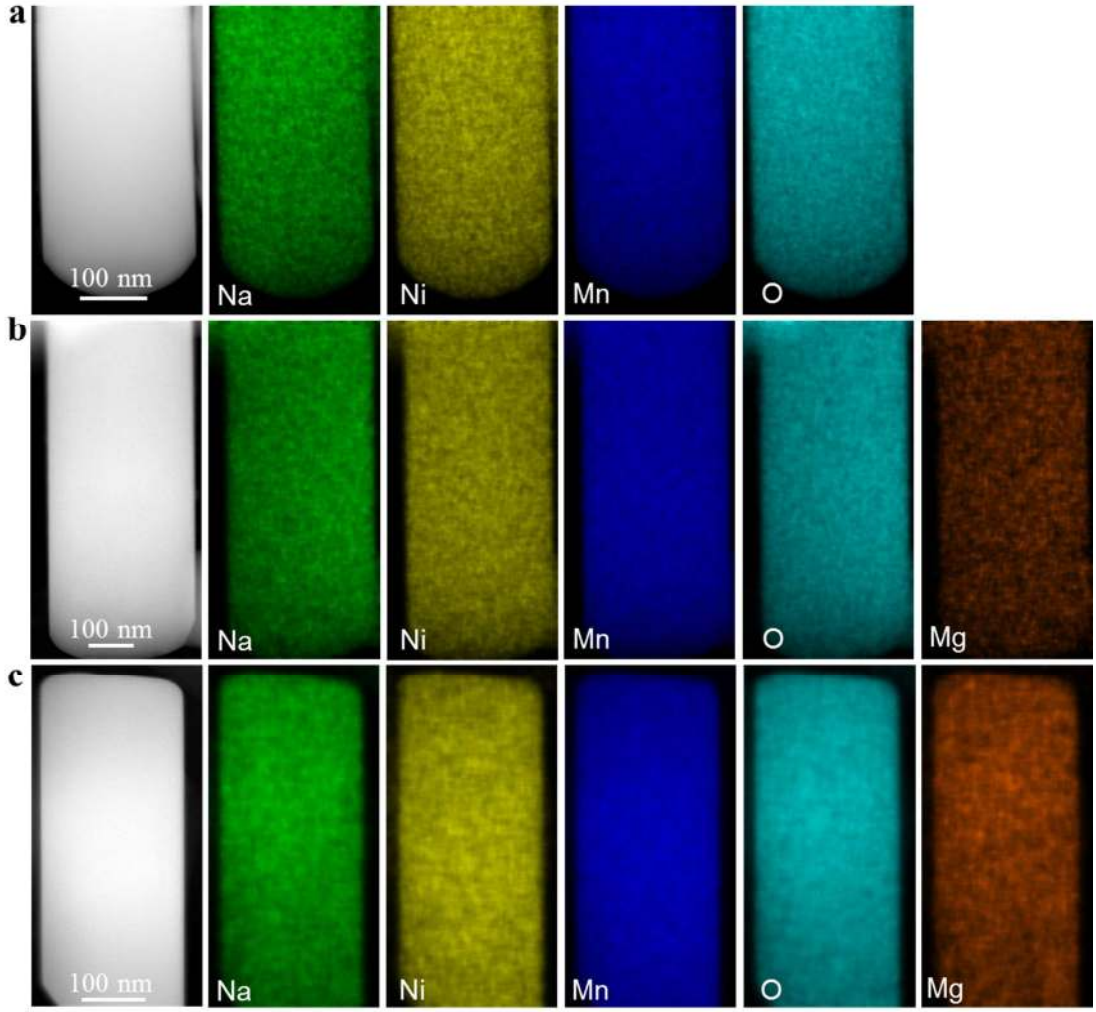

Figure S2. STEM-EDS mappings show that sodium, nickel, manganese, oxygen and magnesium are uniformly distributed in the as-prepared samples. (**a**) P2-NM, (**b**) P2-NMM05 and (**c**) P2-NMM10.

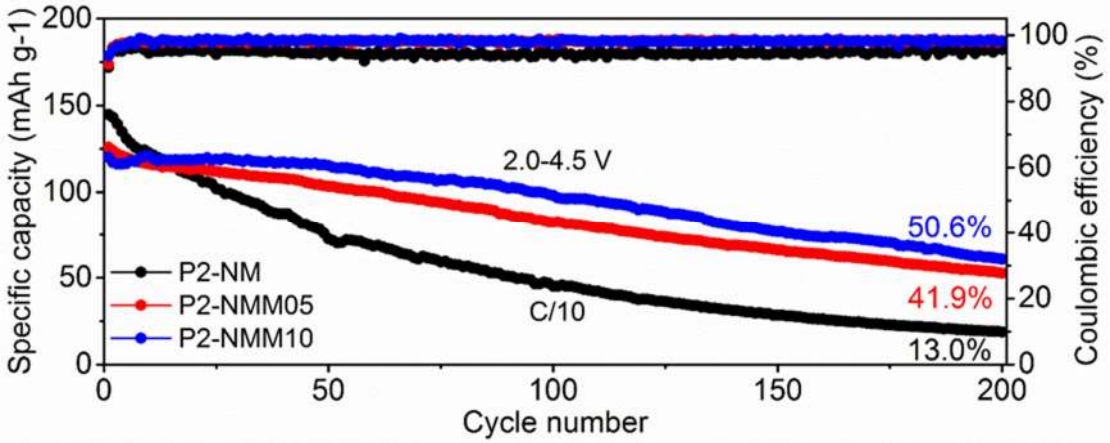

Figure S3. Electrochemical performance of the three P2-structured cathode materials, P2-NM, P2-NMM05 and P2-NMM10 cycled at 2.0-4.5 V after 200 cycles.

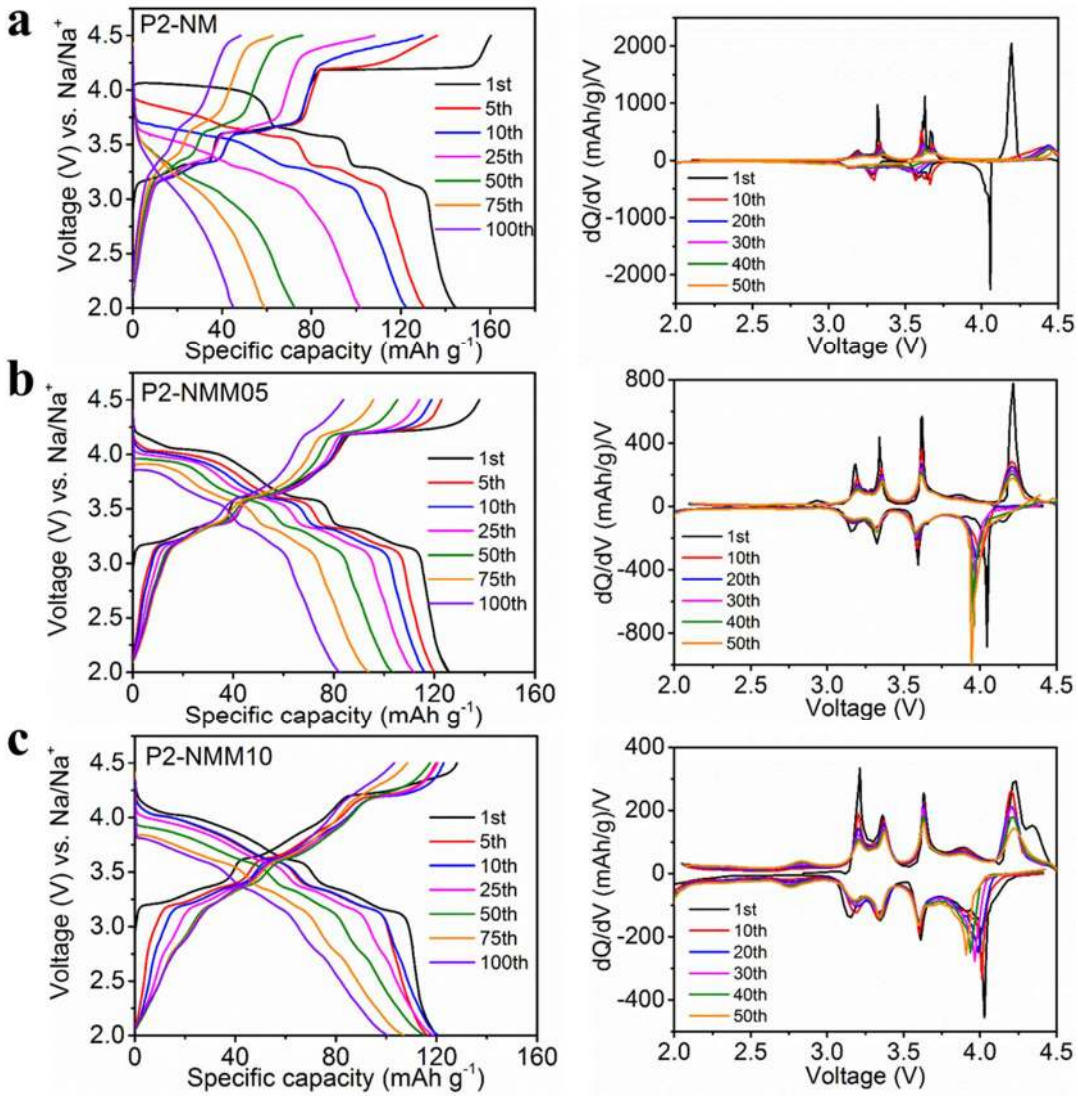

Figure S4. Charge/discharge voltage profiles and corresponding dQ/dV curves of the three cathodes cycled at 2.0-4.5 V. (**a**) P2-NM, (**b**) P2-NMM05 and (**c**) P2-NMM10.

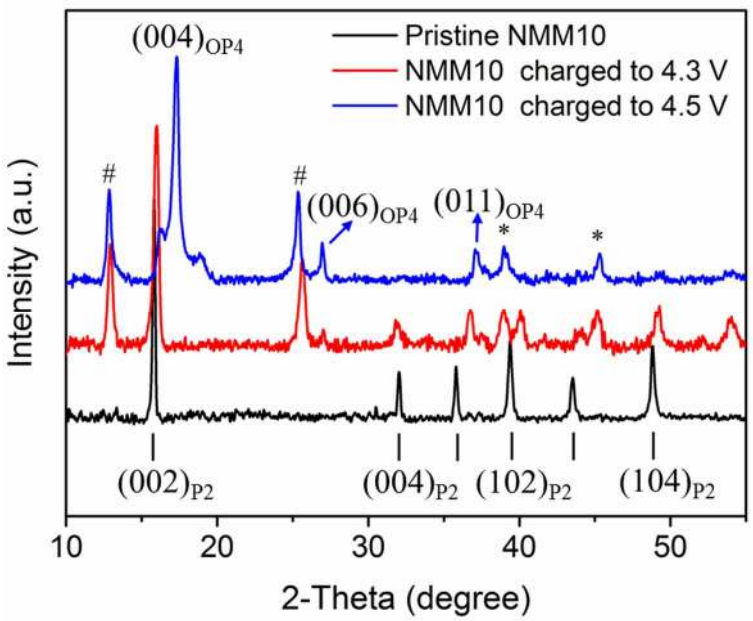

Figure S5. XRD results from the pristine P2-NMM10 and the P2-NMM10 charged to 4.3 V and 4.5 V. # and * represent the peaks from hydrated material and Al foil, respectively.

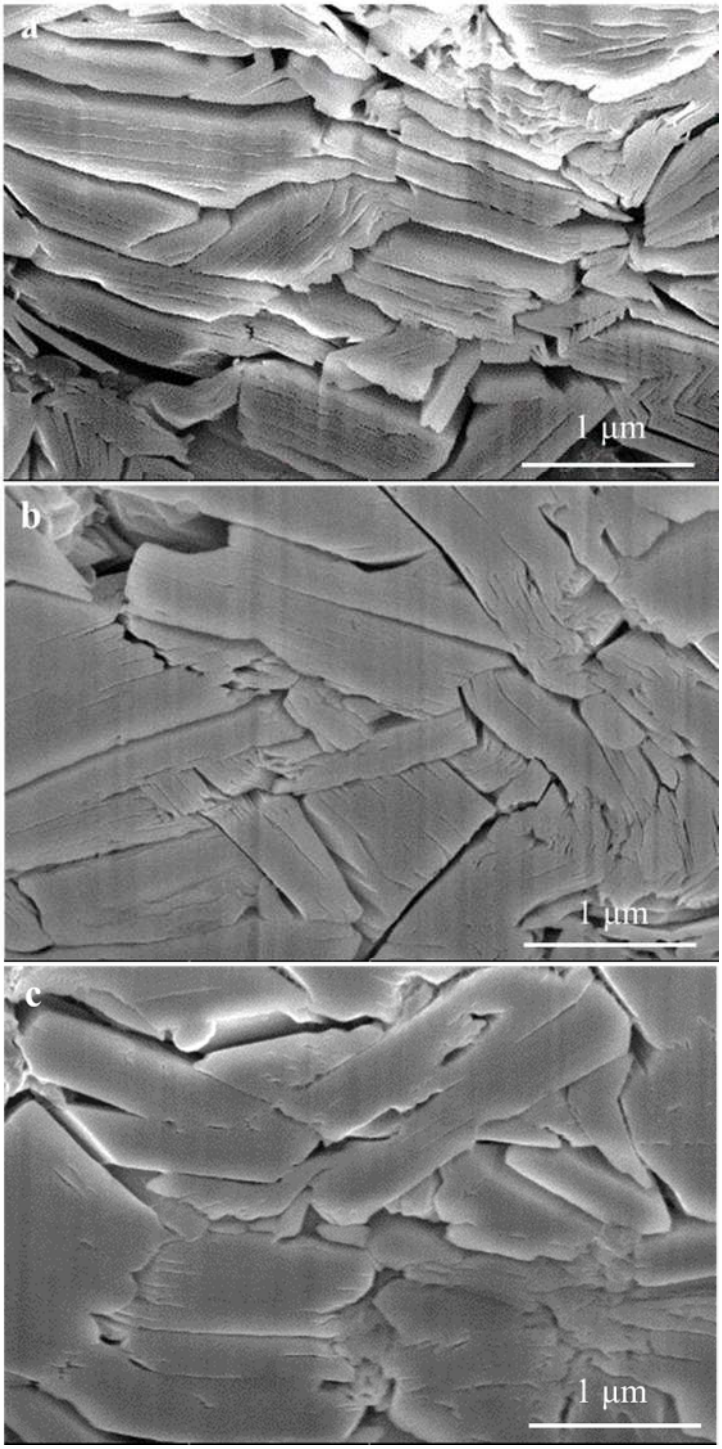

Figure S6. Cross sectional images by SEM. (**a**) P2-NM sample after 50 cycles at 2.0-4.5 V. (**b**) P2-NMM05 sample after 50 cycles at 2.0-4.5 V. (**c**) P2-NMM10 sample after 50 cycles at 2.0-4.5 V. The density of cracks decreases from (**a**) to (**c**).

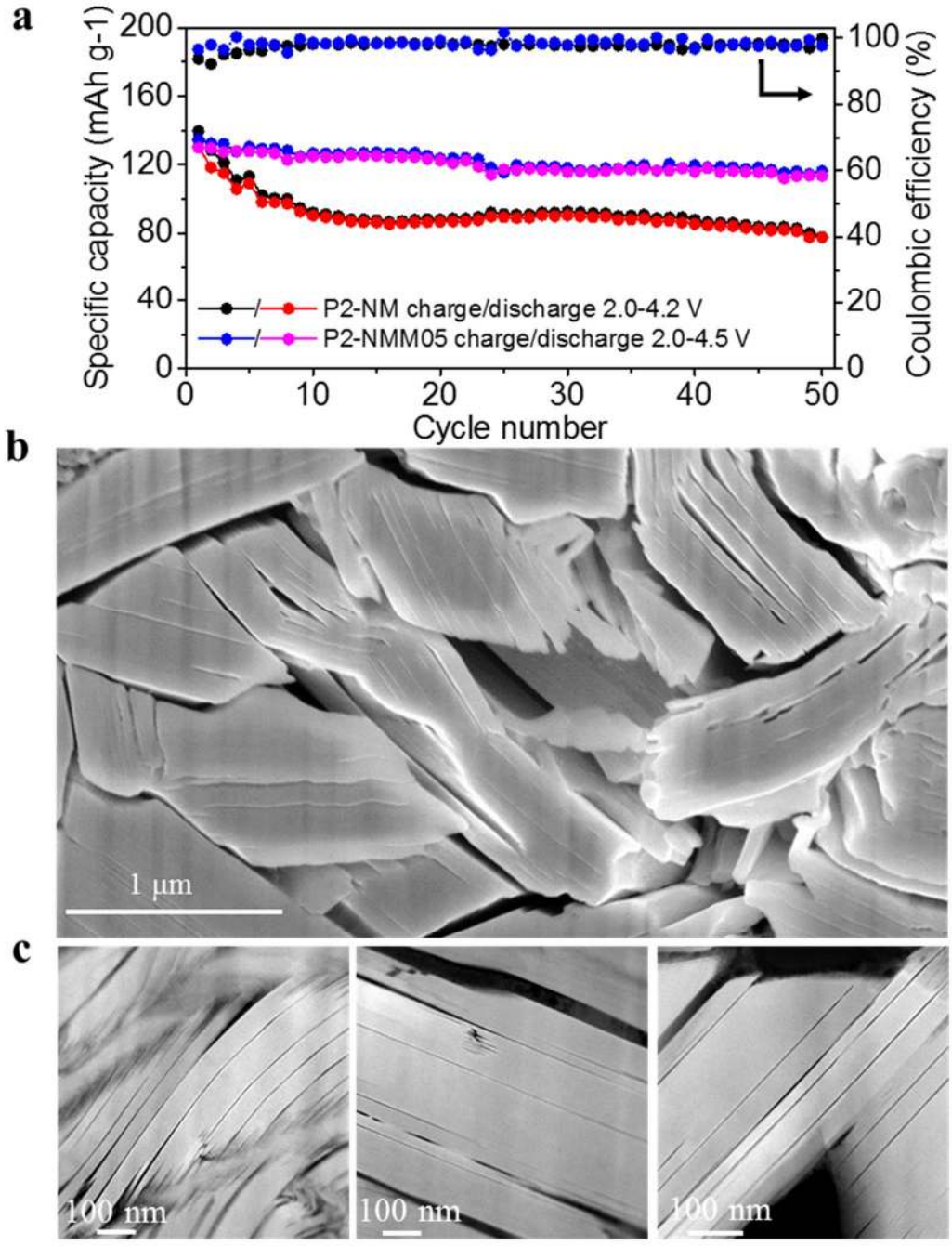

Figure S7. a, Electrochemical performance of P2-NM cycled at 2.0-4.2 V and P2-NMM05 cycled at 2.0-4.5 V, where their initial capacities are comparable. **b**, SEM cross sectional image of the P2-NM cathode after 50 cycles at 2.0-4.2 V. **c**, HAADF cross sectional image of the P2-NM after 50 cycles at 2.0-4.2 V.

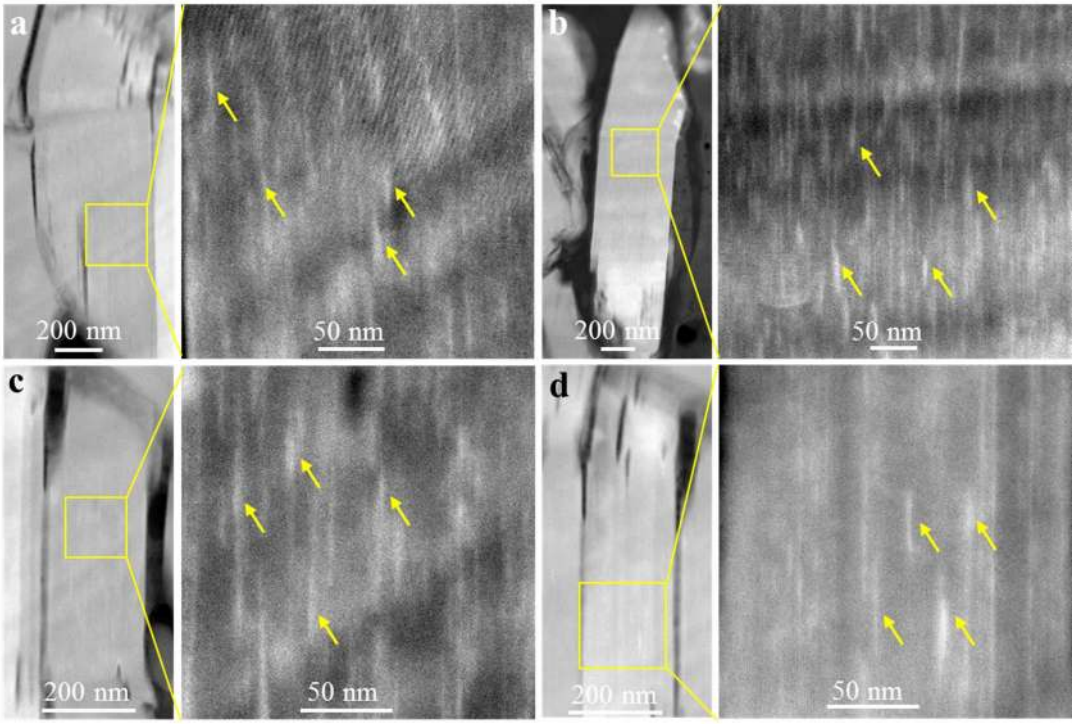

Figure S8. Observing bright stripes (highlighted by yellow arrows) in P2-NMM10 after 50 cycles at 2.0-4.5 V using STEM-HAADF.

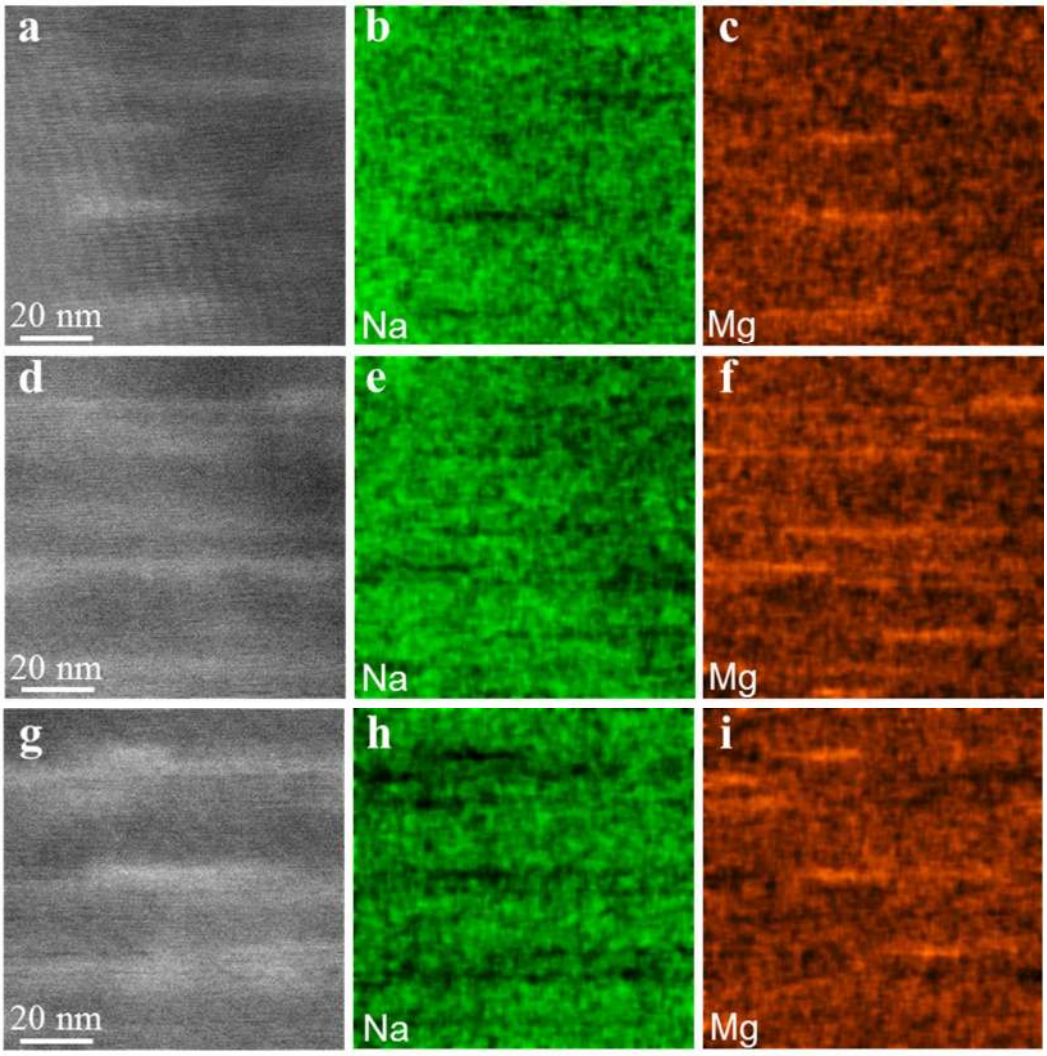

Figure S9. STEM-HAADF images and corresponding EDS of P2-NMM10 after 50 cycles at 2.0-4.5 V, showing that Mg element segregation and Na element deficiency in bright stripes.

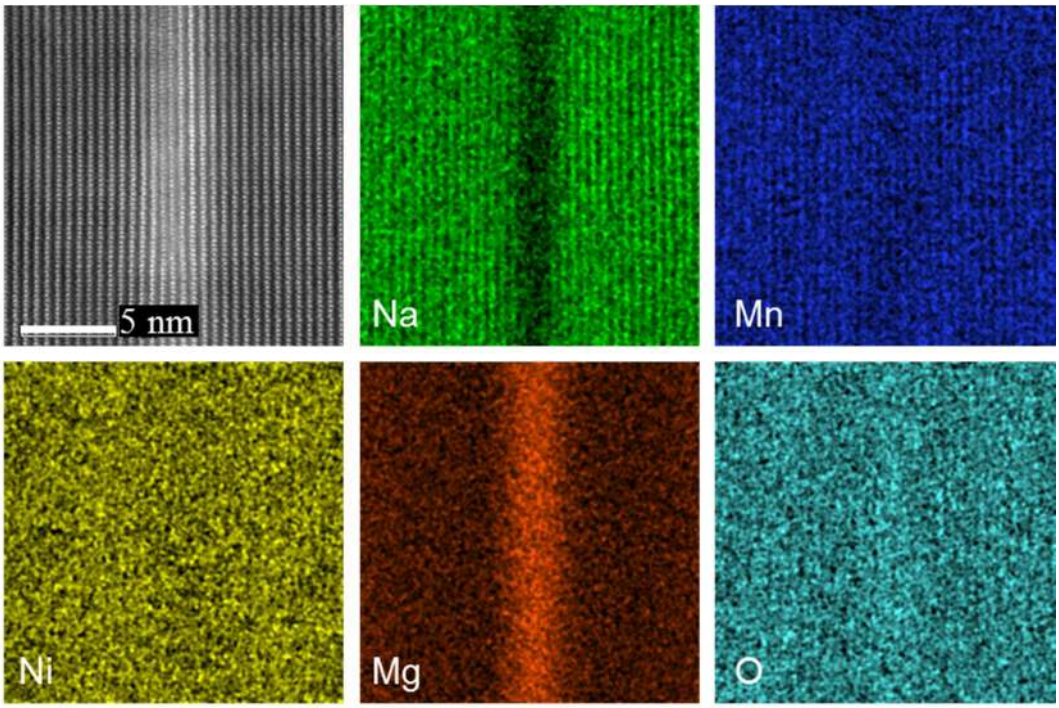

Figure S10. Atomic resolution EDS mappings showing the distributions of sodium, nickel, manganese, oxygen and magnesium in a bright stripe region. The particle is from the P2-NMM10 after 50 cycles at 2.0-4.5 V.

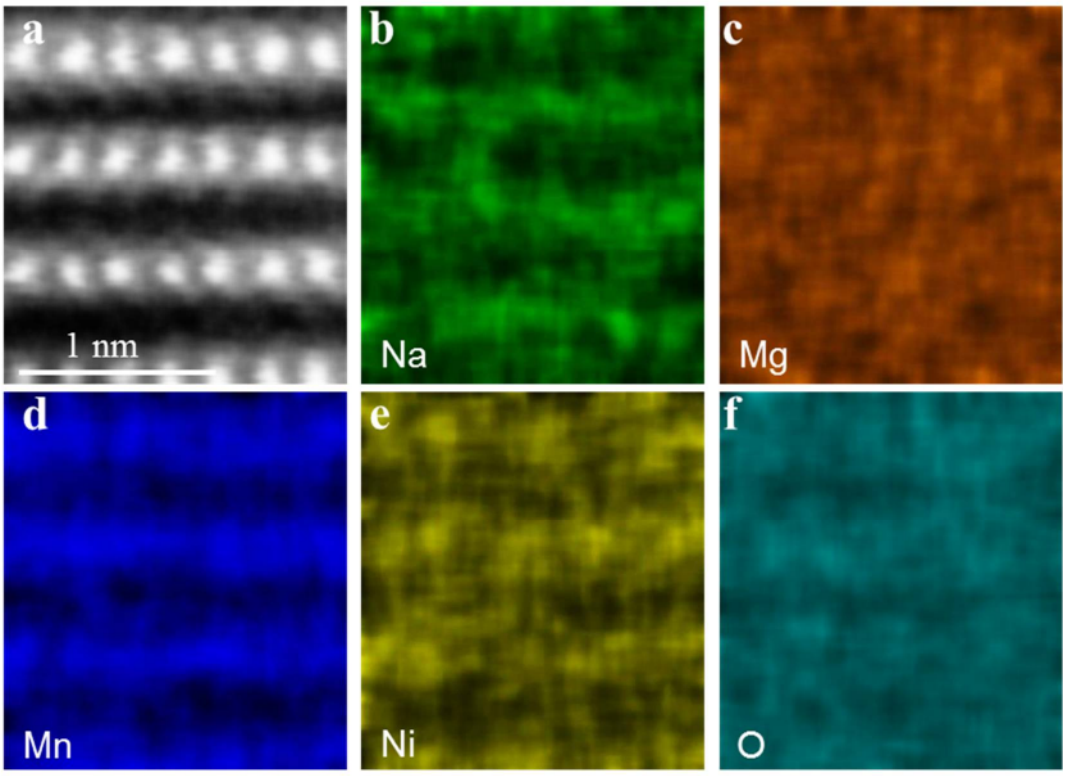

Figure S11. Atomic resolution EDS showing that distribution of sodium, nickel, manganese, oxygen and magnesium in P2-NMM10 before cycling. Magnesium shows no segregation behavior.

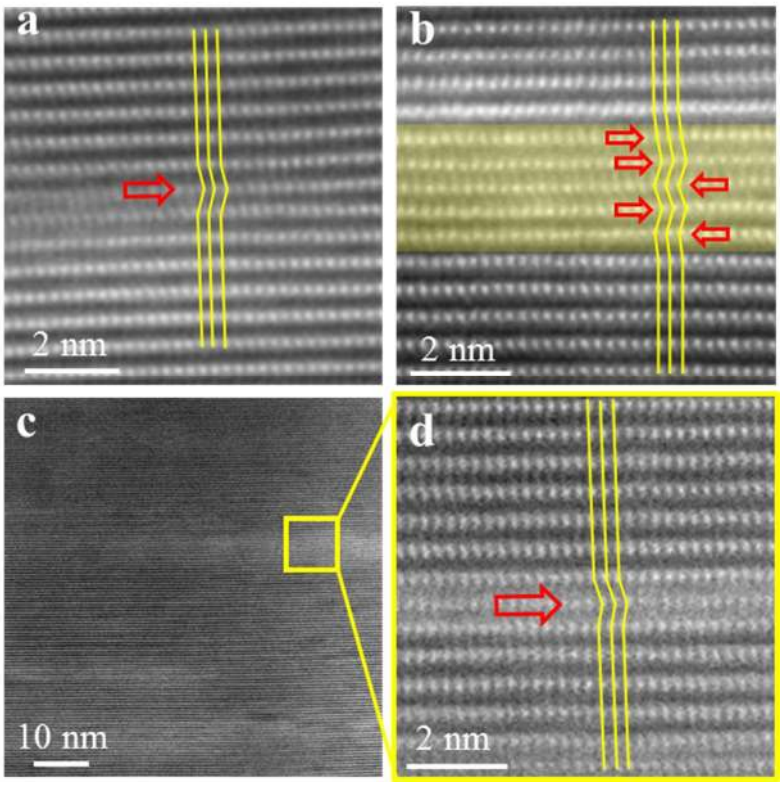

Figure S12. (**a, b**) STEM-HAADF images of precipitates in the P2-NMM10 cathode cycled at 4.5 V. (**c, d**) STEM-HAADF images of precipitates in the P2-NMM05 cycled at 4.5 V. Red arrows indicate the shuffle directions. Yellow lines indicate the stacking sequence changes due to formation of precipitates.

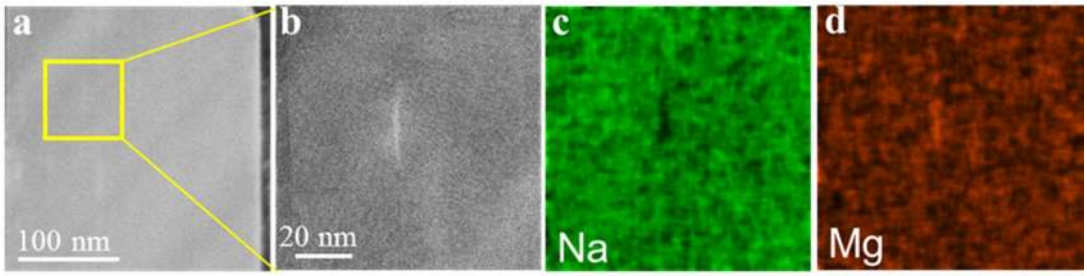

Figure S13. (**a, b**) STEM-HAADF images and EDS mappings (**c**) Na map and (**d**) Mg map in P2-NMM05 after 50 cycles at 2.0-4.5 V. The results show Mg element segregation and Na element deficiency in the bright stripe.

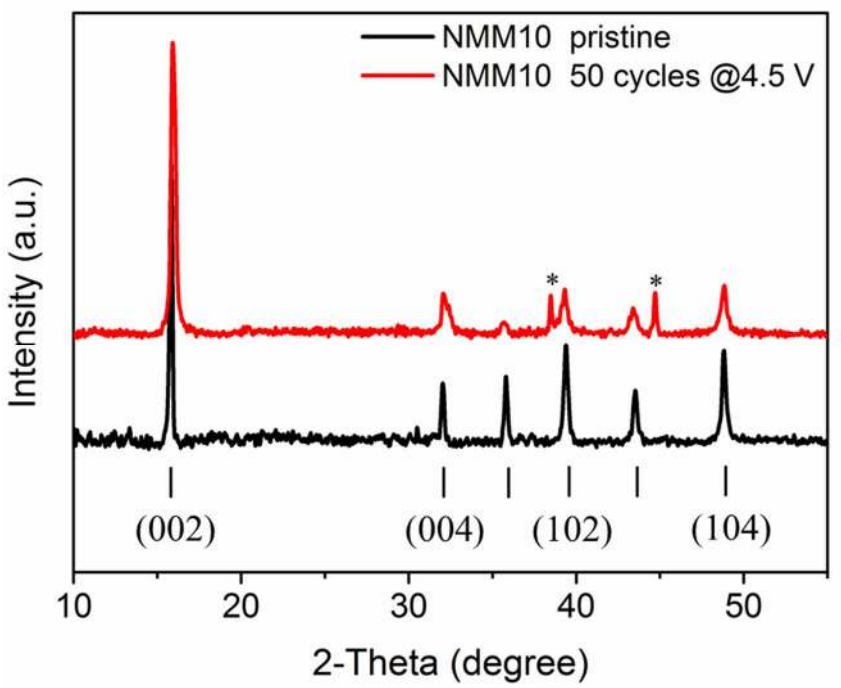

Figure S14. The normalized XRD patterns of the pristine P2-NMM10 and the P2-NMM10 after 50 cycles at 2.0-4.5 V. New phase is not detected after cycling. The intensity variation is probablly due to lattice degradation. * represents the peaks from Al foil.

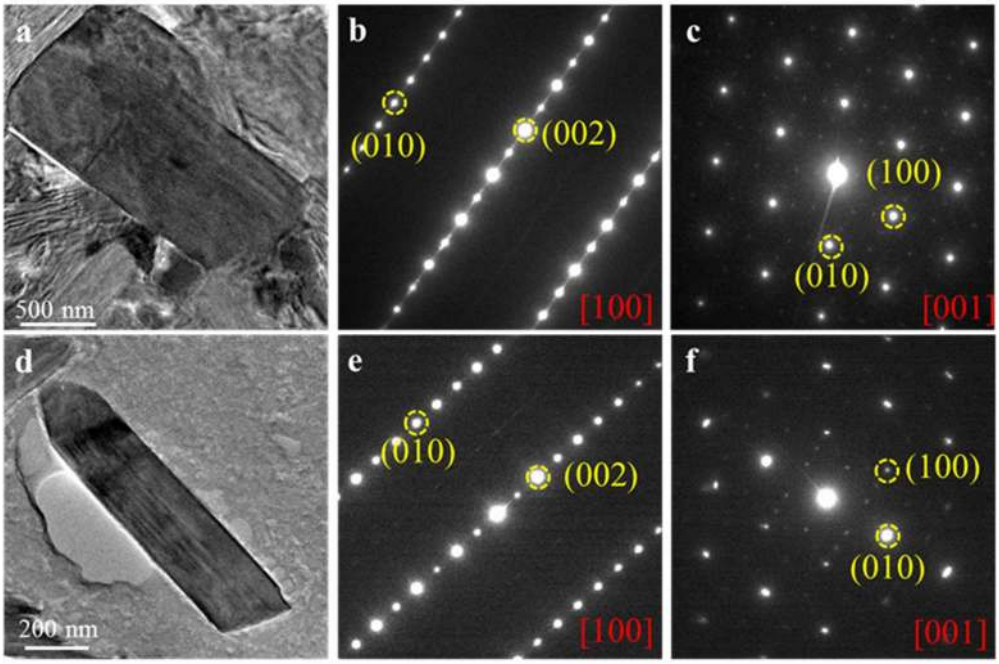

Figure S15. (**a-c**) TEM image and corresponding SAED patterns from the pristine P2-NMM10 cathode. (**d-f**) TEM image and corresponding SAED patterns from the P2-NMM10 cathode cycled at 2.0-4.5 V after 50 cycles. Electron diffraction does not show appreciable difference.

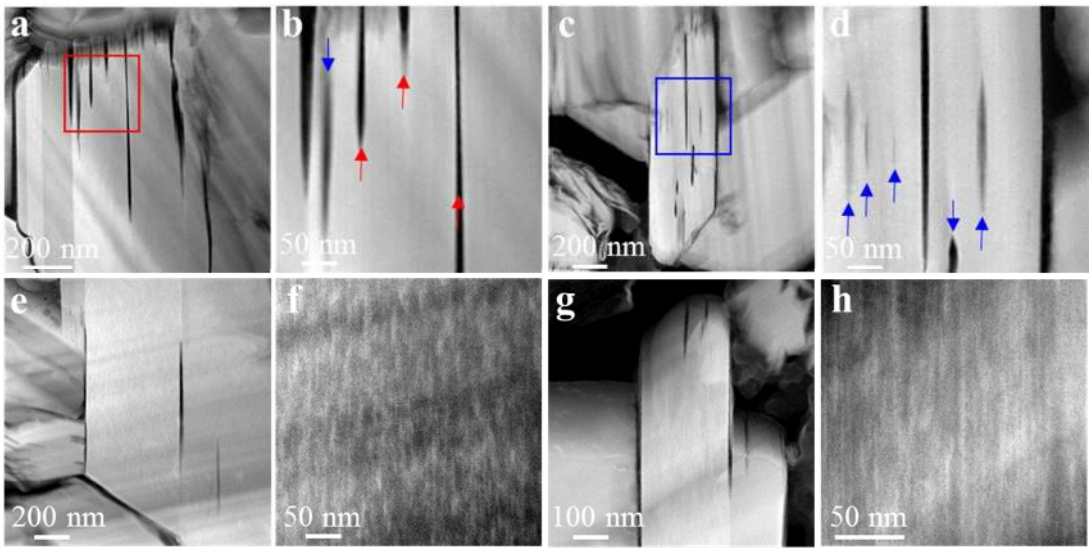

Figure S16. STEM-HAADF observations. (**a-d**) grains from the P2-NMM10 after 100 cycles at 2.0-4.3 V, who have no bright stripes but many cracks. Red arrows in (**b**) highlight the cracks at the surface of the grain from the red frame in (**a**). Blue arrows in (**b**, **d**) highlight the cracks in grain interior. (**e-h**) grains from the P2-NMM10 after 100 cycles at 2.0-4.5 V, who have high density of bright stripes but few cracks.

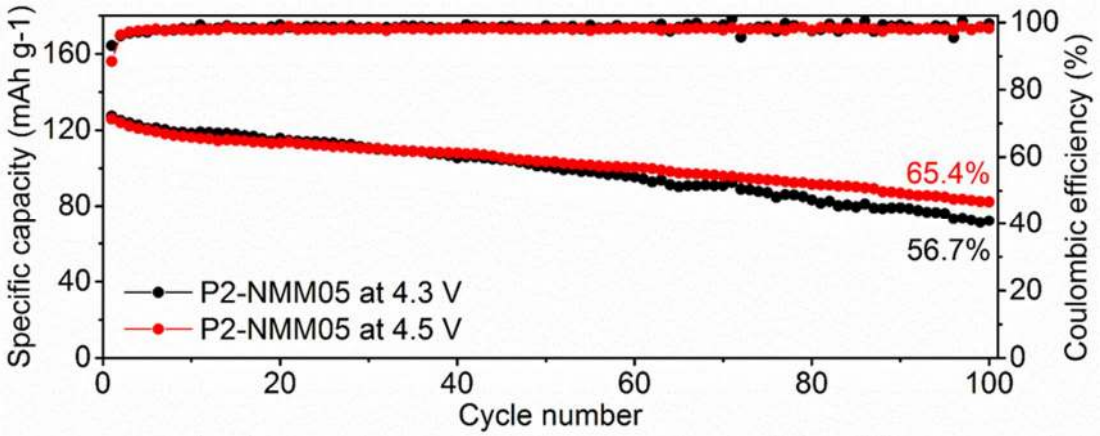

Figure S17. Electrochemical performance of the P2-NMM05 cathode cycled at 2.0-4.3 V and 2.0-4.5 V for 100 cycles. High charge cutoff voltage cycling leads to improved cyclability.

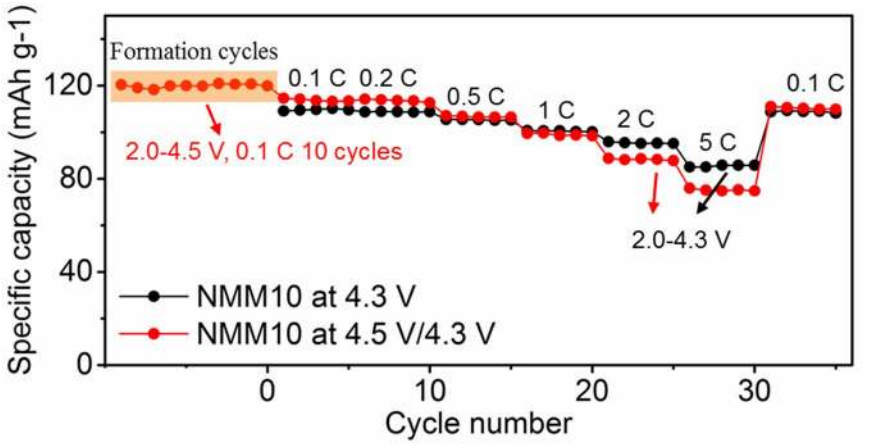

Figure S18. Rate capability of P2-NMM10 at 4.3 V with (red) and without (black) dopant segregation. The pretreatment, 10 cycles at 4.5 V, is designed to form precipitates (colored with orange background).

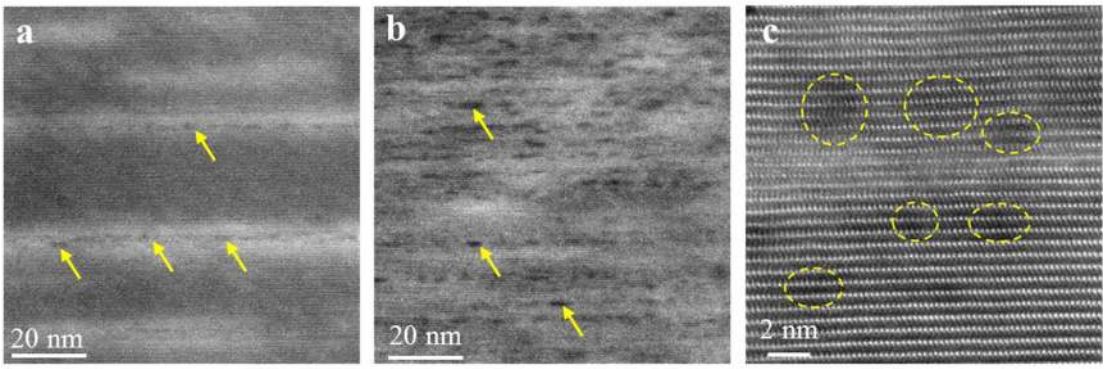

Figure S19. Observing the dark spots by STEM-HAADF imaging. **(a,b),** High density of dark spots are generated in the P2-NMM10 cathode cycled at 2.0-4.5 V after 100 cycles. **c**, Atomic resolution image of the P2-NMM10 cathode cycled at 2.0-4.5 V after 100 cycles. Yellow arrows and dashed yellow circles highlight the dark spots in (**a-c**).

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-$Na_{0.67}Ni_{0.28}Mn_{0.67}Mg_{0.05}O_2$ (P2-NMM05) 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	0.2430
Na_e	2d	0.3333	0.6667	0.25	0.4270
Ni	2a	0	0	0	0.2724
Mn	2a	0	0	0	0.6776
Mg	2a	0	0	0	0.05
O	4f	0.6667	0.3333	0.07992	1.0000
a=2.8941(8) Å	c=11.1667(9) Å	V=81.004(8) $Å^3$	Rp=2.89%	Rwp=4.41%	S=2.7570

Table S3. 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