Supplementary Information (SI) for RSC Advances.
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Cation-Anion Co-Redox Induced High-Capacity Cathode for High Energy Density Sodium-Ion Batteries

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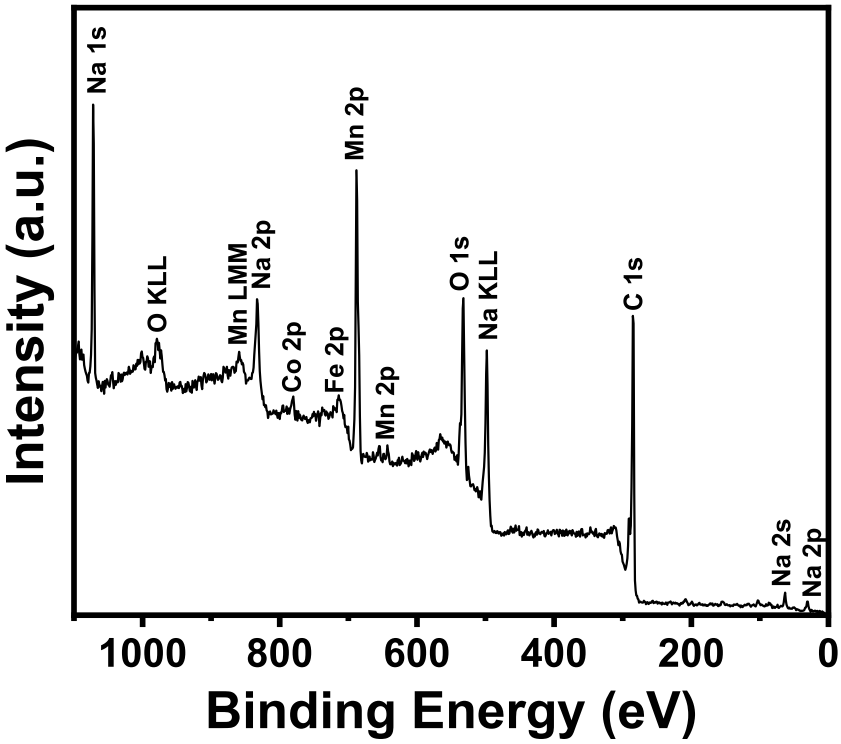

Fig. S1. XPS survey spectrum of the P2-NFMO-CoMgLi cathode material. The carbon signal comes from the conductive adhesive.

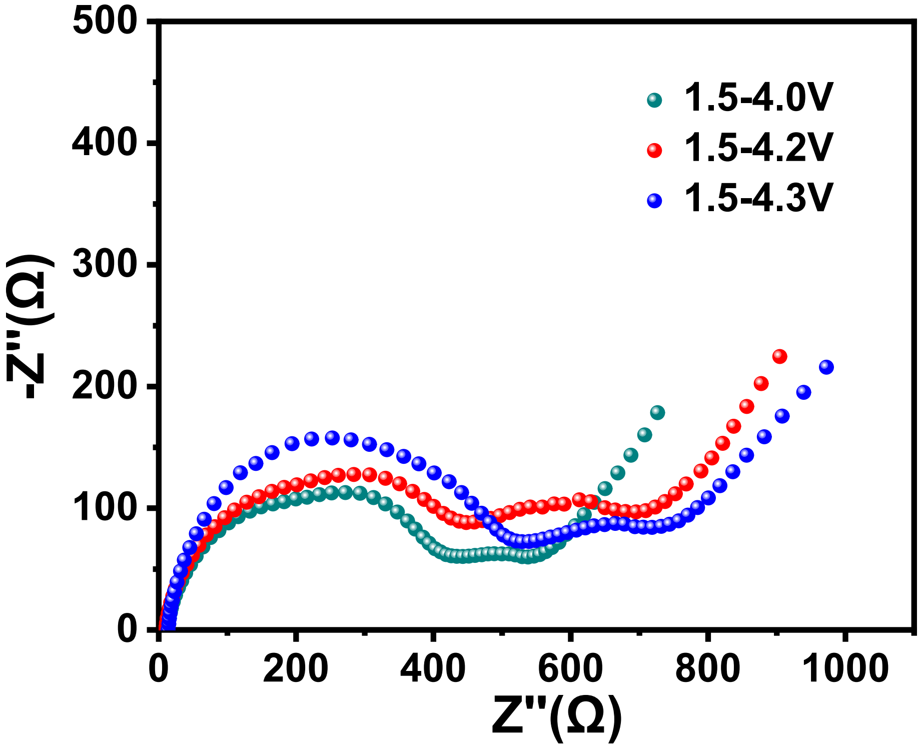

Fig. S2. Nyquist plot of the P2-NCLFMO electrode, along with the simulated curve based on the inset equivalent circuit at charge voltages of 4.0V, 4.2V and 4.3V.

Fig. S2 presents the electrochemical impedance spectrum of P2-NFMO-CoMgLi, which is composed of a semicircle from high to medium frequency followed by a slope line in the low-frequency region. Where the former is related to the charge-transfer resistance (Rct) at the electrode/electrolyte interfaces, the latter refers to the Warburg impedance (Zw) associated with Na+ diffusion in the electrode.

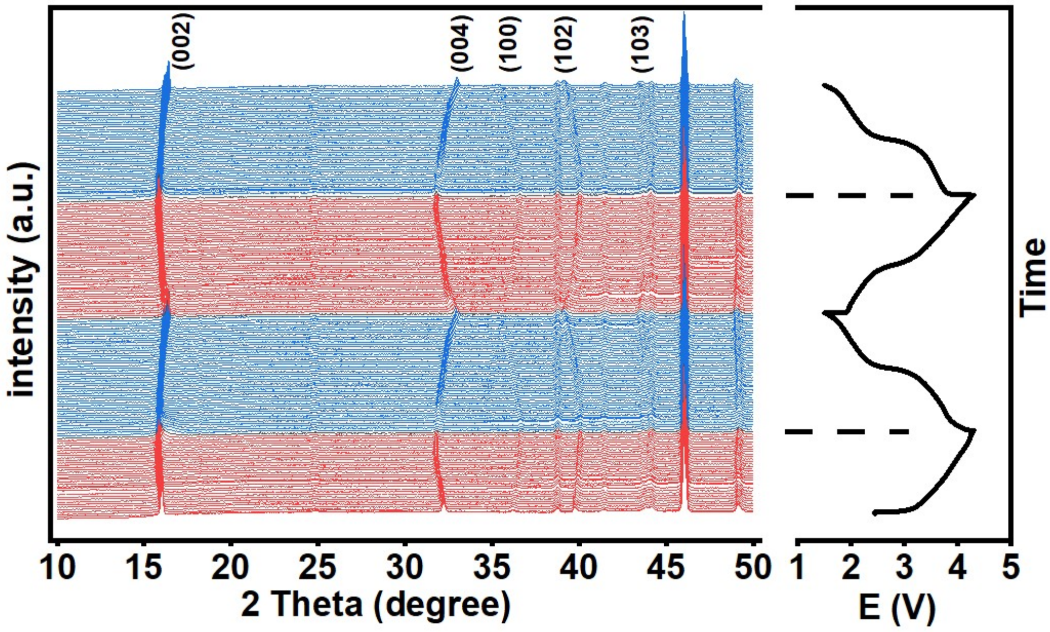

Fig. S3. in situ XRD patterns of the P2-NFMO-CoMgLi electrode during the first two charge/discharge process at 20 mA g^{-1} within the voltage windows 1.5–4.3V .

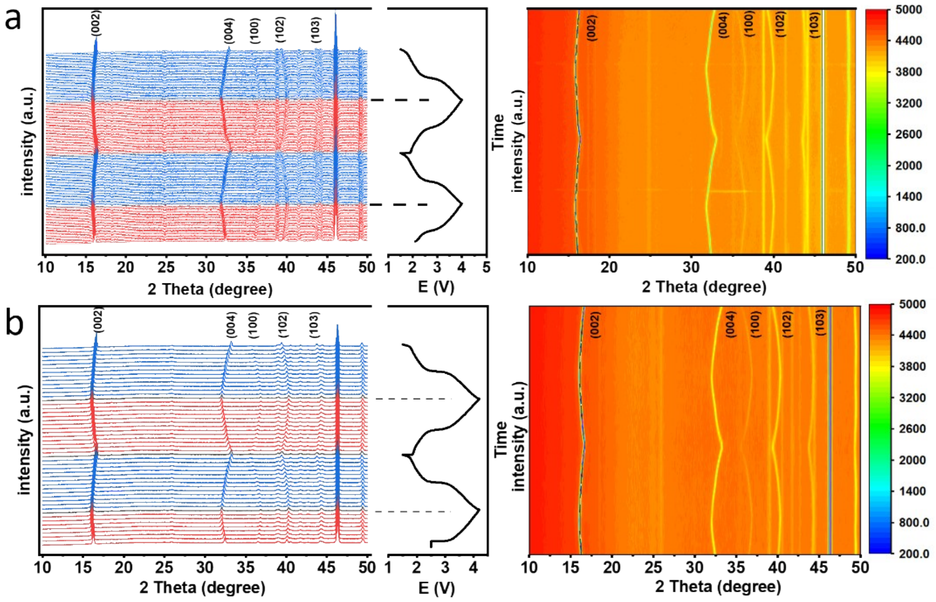

Fig. S4. in situ XRD patterns as well as the corresponding contour plots of the P2-NFMO-CoMgLi electrode during the first two charge/discharge process at 20 mA g^{-1} within the voltage windows (a) 1.5–4.0V and (b) 1.5–4.2V.

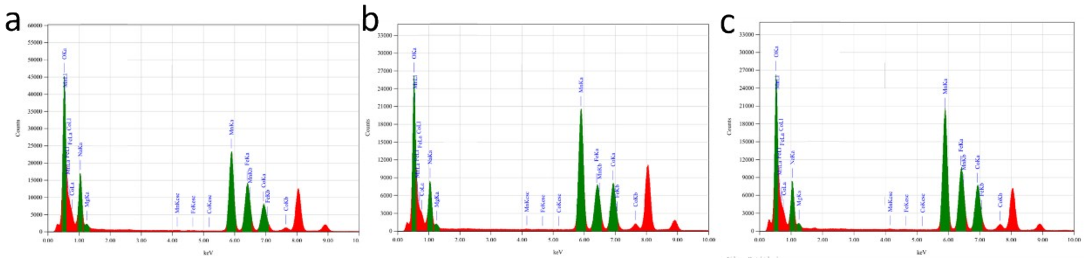

Fig. S5. TEM-EDS spectrum of the P2-NCLFMO cathode material at charge voltages of (a) 4.0 V, (b) 4.2V and (c) 4.3V.

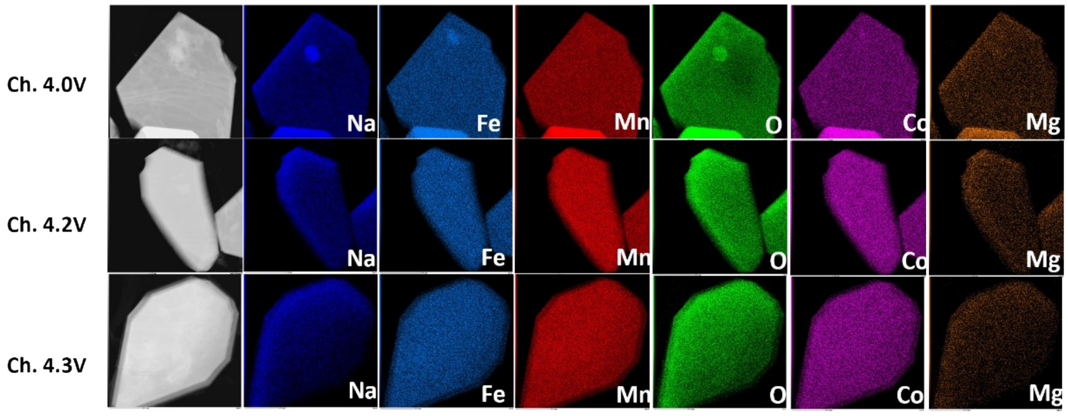

Fig. S6. TEM-EDS mapping images of the P2-NFMO-CoMgLi cathode at charge voltages of 4.0V, 4.2V, and 4.3V.

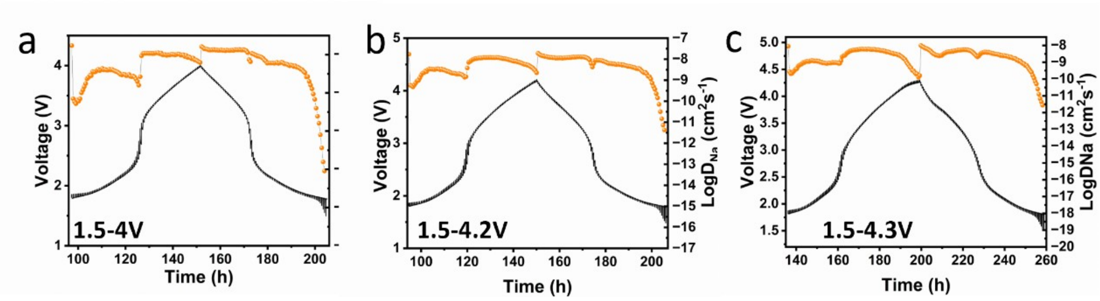

Fig. S7. Charge/discharge GITT curves of the P2-NFMO-CoMgLi cathode at 20 mA g^{-1} within the voltage windows of （a）1.5–4.0V,(b) 1.5–4.2V, and(c) 1.5–4.3V.

Na-ion diffusion coefficient calculation based on the galvanostatic intermittent titration technique (GITT) measurement:

The cell was charged or discharged at 20 mA g^{-1} for 20 min and then relaxed for 80 min to make the voltage reach equilibrium. The Na-ion diffusion coefficients (D) can be calculated based on the simplified equation of

$$D = \frac{4}{\pi}\left(\frac{m_B v_m}{M_B S}\right)^2\left(\frac{\Delta E s}{\Delta E_t}\right)^2\frac{I\tau}{\pi}$$

where τ is the duration time of the current pulse, MB is the molecular weight (g mol^{-1}), mB is the mass of the active material, Vm is the molar volume (cm^3 mol^{-1}), A is the total contact area of electrode and electrolyte, ΔEt is the variation of the cell voltage, and ΔEs is related to the change of steady-state voltage for the corresponding step.

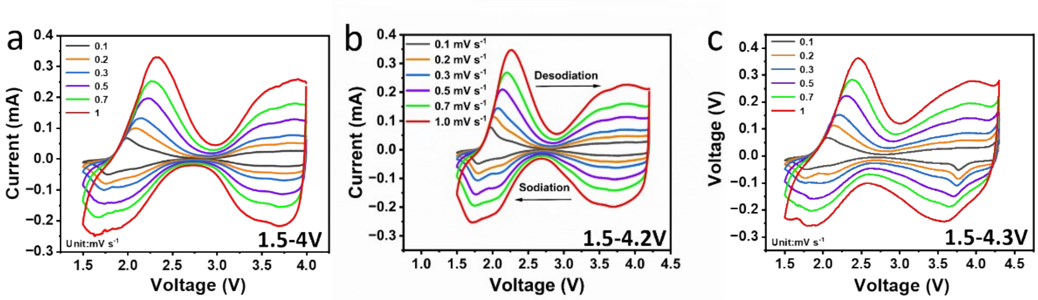

Fig. S8. CV plots at various sweep rates from 0.1 to 1.0 mV s^{-1}within the voltage windows of （a）1.5–4.0V,(b) 1.5–4.2V, and(c) 1.5–4.3V.

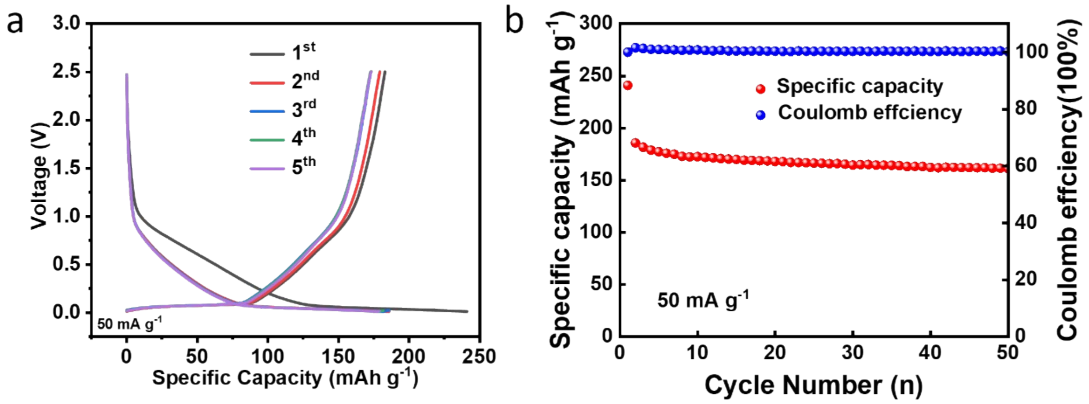

Fig. S9. (a) Galvanostatic charge/discharge profiles and (b) cycling performance of the hard carbon anode at a current density of 50 mA g-1 in the potential range of 0.01-2.5 V vs. Na+/Na.

Table S1. Detailed structural information of P2-NFMO-CoMgLi determined from the Rietveld refined XRD pattern.

Space group=$P6_3/mmc$			R_p=1.27%		R_{wp}=1.69%	
a(Å)=b(Å)=2.8734			c(Å)=11.1989		V(Å)=80.074	
Atom	**Wyckoff position**	**x**	**y**	**z**	**U_{iso}**	**Occ**
O	4f	0.6667	0.3333	0.0920	0.015	1.000
Naf	2b	0.0000	0.0000	0.2500	0.116	0.293
Nae	2d	0.3333	0.6667	0.2500	0.179	0.347
Co	2a	0.0000	0.0000	0.0000	0.018	0.197
Mg	2a	0.0000	0.0000	0.0000	0.018	0.048
Li	2a	0.0000	0.0000	0.0000	0.018	0.018
Fe	2a	0.0000	0.0000	0.0000	0.018	0.200
Mn	2a	0.0000	0.0000	0.0000	0.018	0.508

Table S2. ICP-MS results of the as-prepared $Na_{0.73}Fe_{0.2}Mn_{0.52}Co_{0.2}Mg_{0.05}Li_{0.03}O_2$ cathode.

Elements	Content (mg/kg)	wt.%	molar ratio
Na	138719.1	23.922	0.729
Mn	236475.9	40.780	0.518
Fe	95156.05	16.410	0.205
Co	98146.94	16.925	0.201
Mg	10013	1.727	0.050
Li	1365.41	0.235	0.026

Table S3. The elemental composition of the P2-NFMO-CoMgLi cathode material at different charge voltages was obtained through TEM-EDS spectroscopy.

	Ch. 4.0V		Ch. 4.2V		Ch. 4.3V	
Element	Mass%	Atom%	Mass%	Atom%	Mass%	Atom%
O	6.28	18.42	4.91	14.89	4.52	13.83
Na	0.49	1.00	0.31	0.66	0.30	0.64
Mg	1.58	3.04	1.29	2.58	1.31	2.64
Mn	52.81	45.10	62.67	55.42	56.90	50.74
Fe	34.29	28.81	22.97	19.98	31.03	27.22
Co	4.55	3.62	7.85	6.47	5.94	4.93

Table S4. ICP-MS results of the as-prepared $Na_{0.73}Fe_{0.2}Mn_{0.52}Co_{0.2}Mg_{0.05}Li_{0.03}O_2$ cathode at charge voltages of 4.0V.

Elements	Content (mg/kg)	wt.%	molar ratio
Na	132548.544	22.723	0.678
Mn	242135.922	41.512	0.518
Fe	96092.233	16.473	0.199
Co	99781.553	17.116	0.201
Mg	10339.806	1.775	0.051
Li	2427.184	0.426	0.031

Table S5. ICP-MS results of the as-prepared $Na_{0.73}Fe_{0.2}Mn_{0.52}Co_{0.2}Mg_{0.05}Li_{0.03}O_2$ cathode at charge voltages of 4.2V.

Elements	Content (mg/kg)	wt.%	molar ratio
Na	120218.3	22.221	0.657
Mn	227442.8	42.041	0.520
Fe	89241.16	16.500	0.200
Co	92879.42	17.168	0.198
Mg	9459.459	1.748	0.050
Li	1767.152	0.327	0.032

Table S6. ICP-MS results of the as-prepared $Na_{0.73}Fe_{0.2}Mn_{0.52}Co_{0.2}Mg_{0.05}Li_{0.03}O_2$ cathode at charge voltages of 4.3V.

Elements	Content (mg/kg)	wt.%	molar ratio
Na	114464.4	21.346	0.628
Mn	226391.8	42.218	0.519
Fe	90151.52	16.812	0.203
Co	94133.19	17.554	0.201
Mg	9654.686	1.800	0.051
Li	1444.679	0.269	0.026