Supplementary Information (SI) for Nanoscale.
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Supporting Information for

In-intercalation and Si-containing protective layer enhance electrochemical performance of $NaNi_{0.5}Mn_{0.5}O_2$ for sodium-ion batteries

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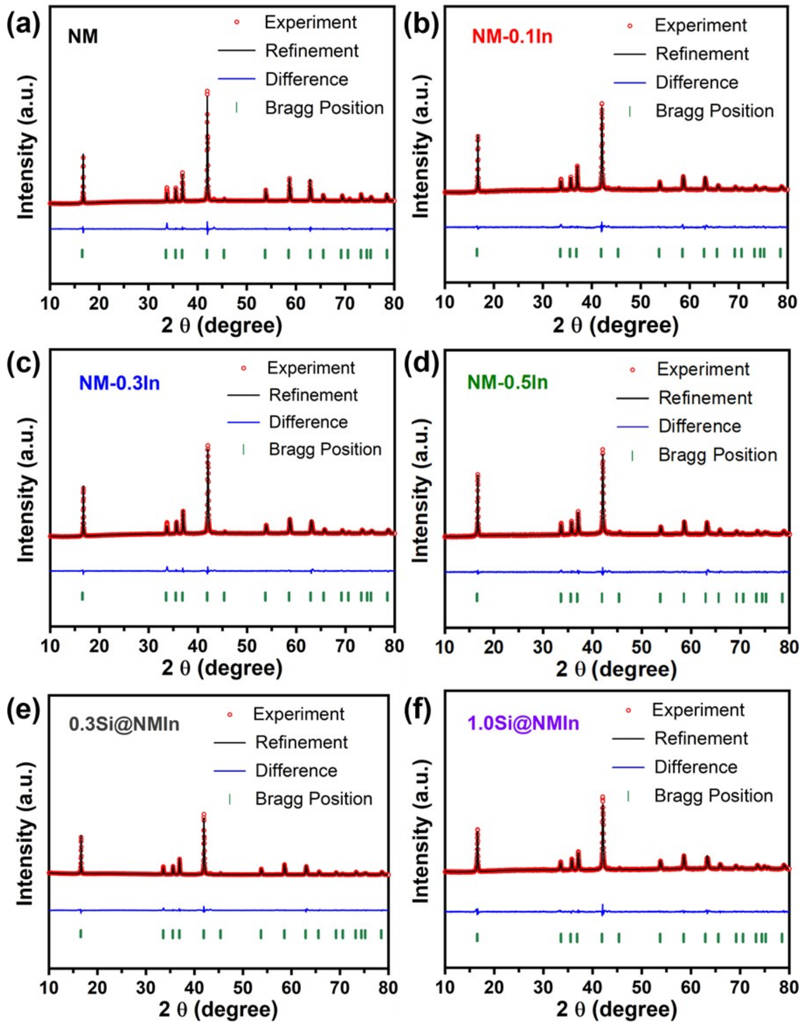

Fig. S1 Rietveld refinement profiles of (a) NM, (b-d) modified with different In contents intercalation and (e, f) Si@In-doping samples.

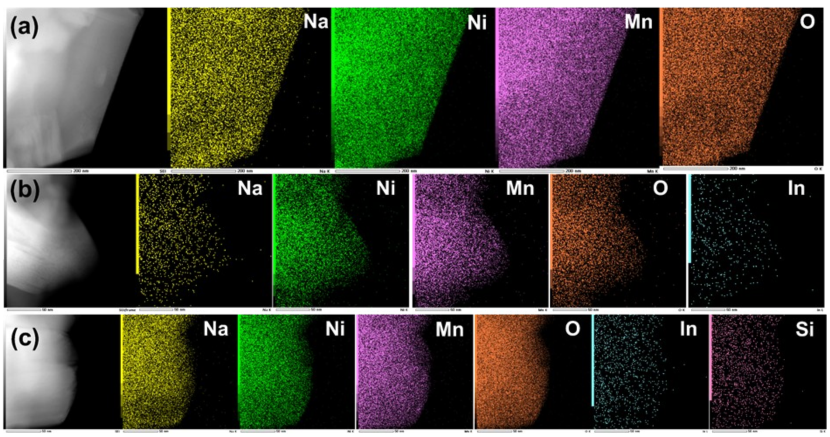

Fig. S2 TEM elemental mappings of Na, O, Mn, Ni, In and Si of (a) NM, (b) NM-0.3In and (c)0.5Si@NMIn

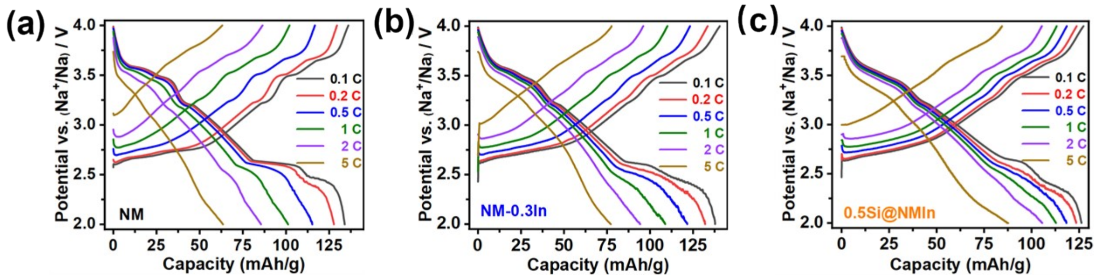

Fig. S3 The charge-discharge curves of (a) the NM55, (b) the NM-0.3In and (c) the 0.5Si@NMIn at 2.0-4.0 V and 25 °C under different rates.

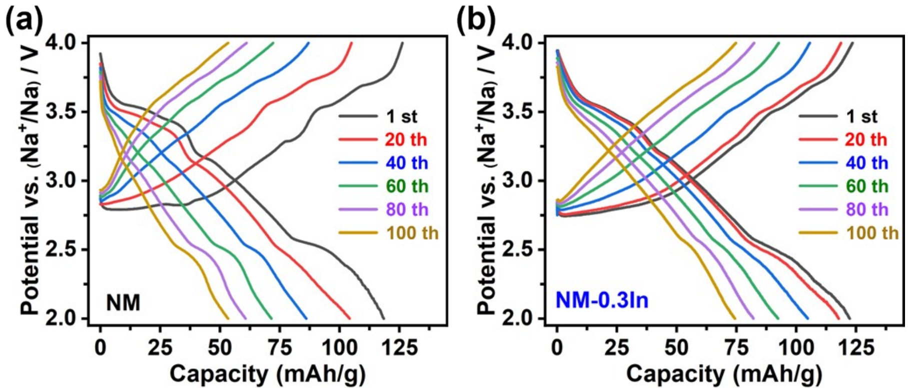

Fig. S4 The galvanostatic charge-discharge (GCD) curves of (a) NM, (b) NM-0.3In.

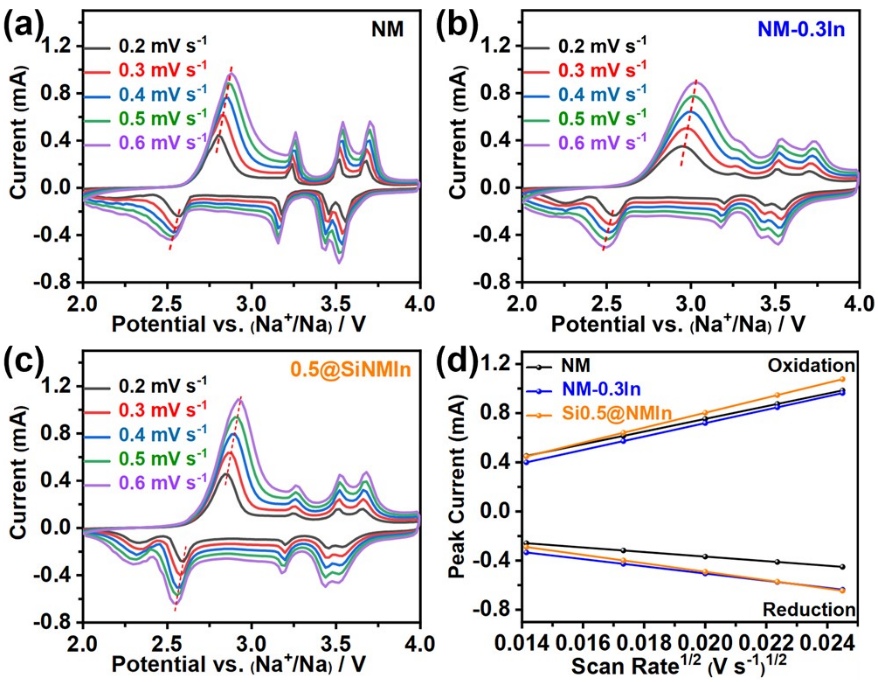

Fig. S5 CV tests of (a) NM, (b) NM-0.3In and (c) 0.5Si@NMIn at the different scan rates. (d) The linear fitting of the peak currents of oxidation/reduction peaks at different scan rates with the square root of the scan rates.

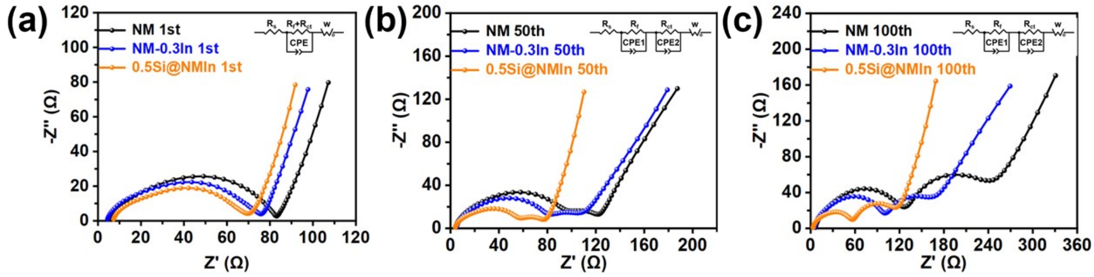

Fig. S6 The Nyquist plots of NM, NMIn-0.3 and 0.5Si@NMIn cathodes in the (a) 1st, (b) 50th and (c) 100th over 2.0-4.0 V.

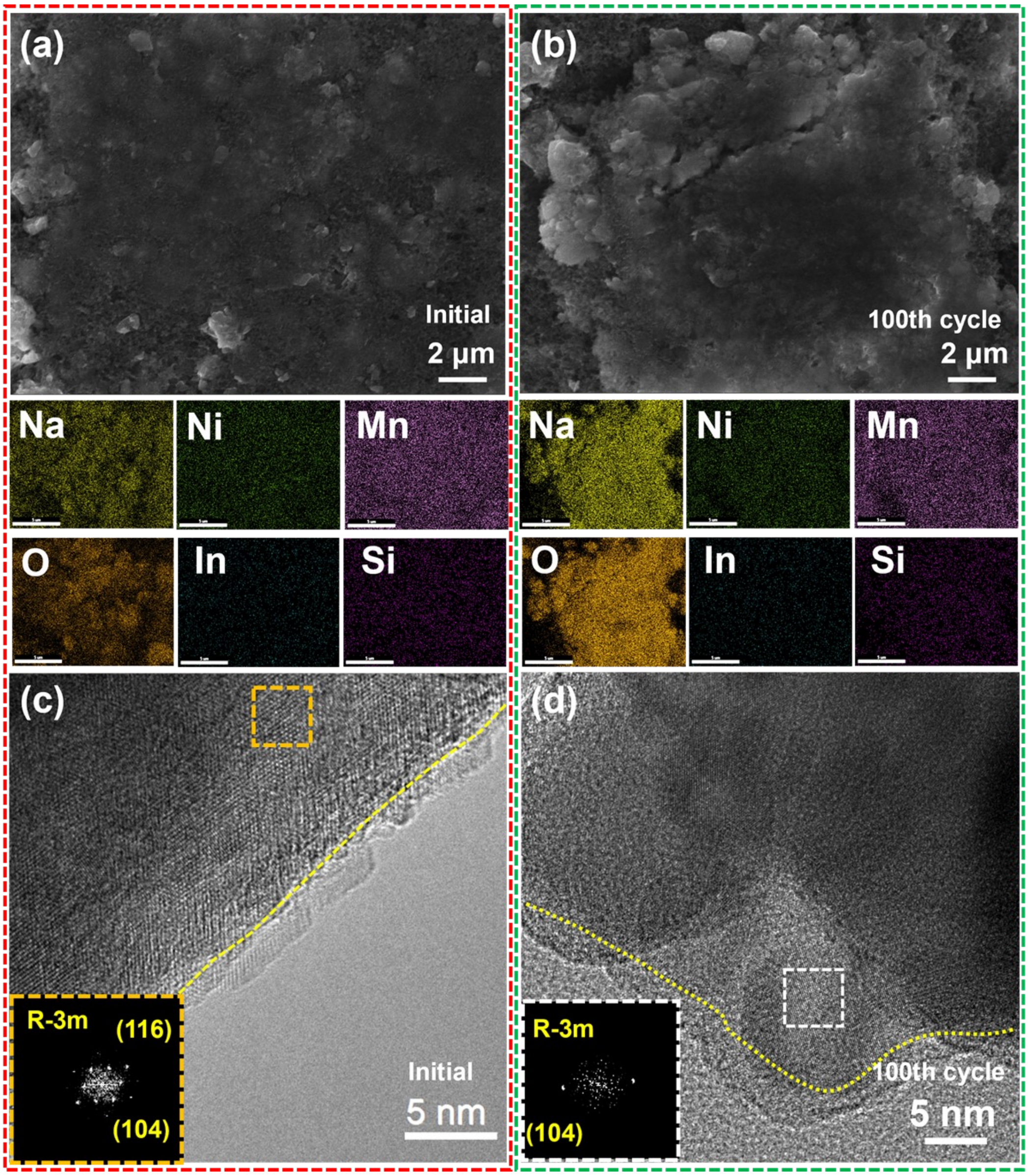

Fig. S7 SEM images of (a) the initial pole piece of 0.5Si@NMIn and (b) the spent pole piece of 0.5Si@NMIn experienced 100 cycles at 1 C. TEM images of (c) the fresh 0.5Si@NMIn and (d) the spent 0.5Si@NMIn experienced 100 cycles at 1 C.

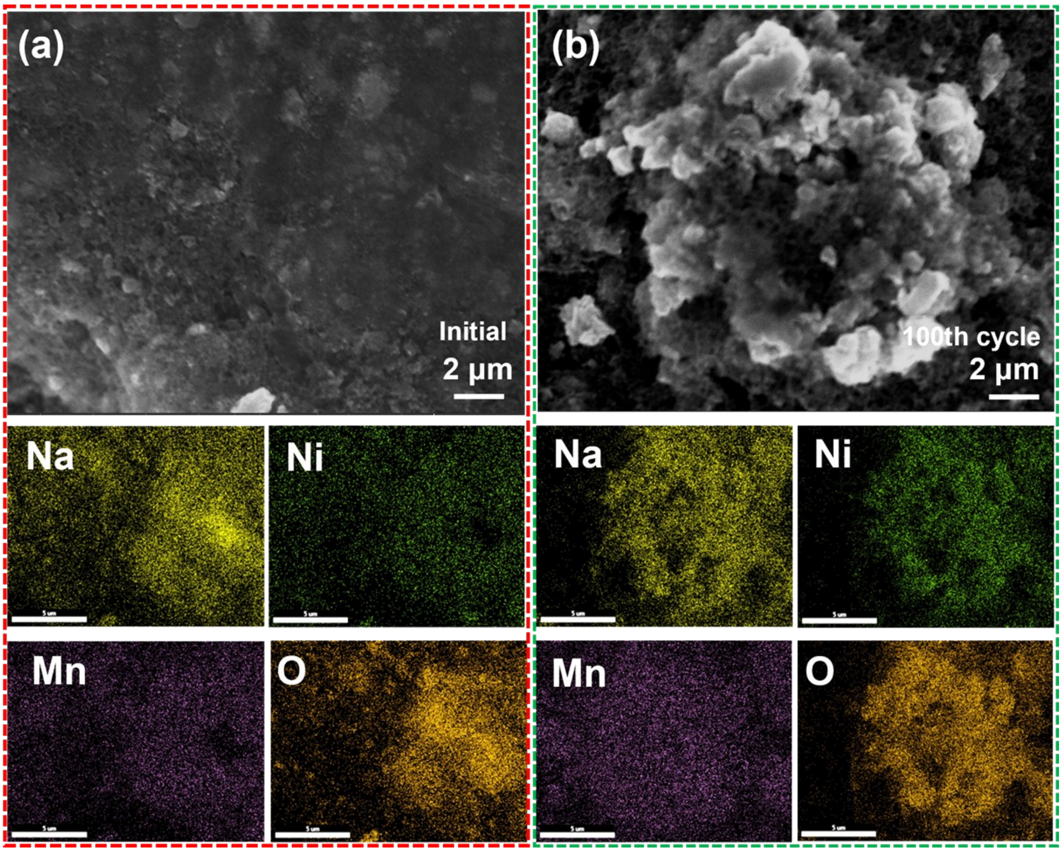

Fig. S8 SEM images of (a) the initial pole specie of NM and (b) the spent pole specie of NM experienced 100 cycles at 1 C.

Table S1 Relative percentages and binding energies of Ni^{2+}/Ni^{3+} in Ni 2p XPS spectra.

Sample	Ni $2p_{3/2}$ (eV)		Ni $2p_{1/2}$ (eV)		Ni content (%)	
	Ni^{2+}	Ni^{3+}	Ni^{2+}	Ni^{3+}	Ni^{2+}	Ni^{3+}
NM	854.46	856.15	871.91	873.72	82.60	17.40
NM-0.3In	854.56	856.25	872.11	874.55	79.38	20.62
0.5Si@NMIn	854.79	856.58	872.42	874.65	75.65	24.35

Table S2 Relative percentages and binding energies of Mn^{3+}/ Mn^{4+} in Mn 2p XPS spectra.

Sample	Mn $2p_{3/2}$ (eV)		Mn $2p_{1/2}$ (eV)		Mn content (%)	
	Mn^{3+}	Mn^{4+}	Mn^{3+}	Mn^{4+}	Mn^{3+}	Mn^{4+}
NM	641.53	643.50	652.49	653.79	65.90	34.10
NM-0.3In	641.62	643.52	653.08	653.96	59.68	40.32
0.5Si@NMIn	641.85	643.66	653.03	654.01	57.37	42.63

Table S3 Relative percentages and binding energies of oxygen species in O 1s XPS spectra.

Sample	Adsorbed O		O Vacancy		Lattice O	
	O 1s (eV)	O content (%)	O 1s (eV)	O content (%)	O 1s (eV)	O content (%)
NM	528.75	11.18	530.93	77.98	535.27	10.84
NM-0.3In	528.81	9.95	530.98	79.16	535.31	10.89
0.5Si@NMIn	529.43	8.51	531.22	78.51	535.66	12.98

Table S4 Na^+ diffusion coefficient (D_{Na^+}) of NM, NM-0.3In and 0.5Si@NMIn.

Sample	D_{Na^+} (cm^2 s^{-1})	
	Desodiation	Sodiation
NM	3.48×10^{-11}	4.55×10^{-12}
NM-0.3In	3.65×10^{-11}	8.90×10^{-12}
0.5Si@NMIn	4.76×10^{-11}	1.12×10^{-11}

Table S5 EIS fitting results of NM, NM-0.3In and 0.5Si@NMIn.

Sample	Cycle	R_s (Ω)	R_f+R_{ct} (Ω)
NM	1^{st}	4.14	80.82
	50^{th}	2.93	128.45
	100^{th}	5.08	265.4
NM-0.3In	1^{st}	3.63	69.7
	50^{th}	3.42	118.38
	100^{th}	3.58	170.22
0.5Si@NMIn	1^{st}	6.15	63.78
	50^{th}	3.15	97.20
	100^{th}	1.86	124.87

Table S6 Resistivity and conductivity results of NM, NM-0.3In and 0.5Si@NMIn.

Sample	Pressure (Mpa)	Resistivity (kΩ m)	Conductivity (S m^{-1})
NM	2	30.70	3.26×10^{-5}
	3	28.85	3.47×10^{-5}
	4	27.05	3.70×10^{-5}
NM-0.3In	2	27.91	3.58×10^{-5}
	3	26.02	3.84×10^{-5}
	4	24.11	4.15×10^{-5}
0.5Si@NMIn	2	22.98	4.35×10^{-5}
	3	20.87	4.79×10^{-5}
	4	18.91	5.29×10^{-5}

Galvanostatic intermittent titration technique (GITT) measurement in the 1st cycle and 100th cycle are utilized to determine the Na^+ diffusion coefficient (D_{Na+}) within NM, NM-0.3In and 0.5Si@NMIn cathodes. The D_{Na+} value can be derived using the following formula:

$$D_{Na^+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B A}\right)^2\left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \quad \text{(S1)}$$

Where τ(s) represents the galvanostatic current pulse time, V_M, M_B, and m_B are the molar volume (obtained from the Rietveld refinement results from GSAS II), molecular weight, and the molar mass of the active material, respectively. Meanwhile, A signifies the electrode surface area, ΔE_τ and ΔE_s is the voltage change during the constant current pulse and the corresponding relaxation process.