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Supplementary Information

Simultaneous MgO coating and Mg doping of Na[$Ni_{0.5}Mn_{0.5}$]O_2 cathode: facile and customizable approach to high-voltage sodium-ion batteries

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Experimental Method

Material synthesis

Spherical $[Ni_{0.5}Mn_{0.5}](OH)_2$ precursors were synthesized using the co-precipitation method. The appropriate amounts of $NiSO_4$ and $MnSO_4 \cdot H_2O$ were used as starting materials for the preparation of $[Ni_{0.5}Mn_{0.5}](OH)_2$. The solution concentration (2 mol L^{-1} for the metal solution), pH (~11.0), temperature (50 °C), and stirring speed of the mixture in the batch-type reactor were carefully controlled. The precursor powders were obtained by filtering, washing, and vacuum drying at 110 °C overnight. For $Na[Ni_{0.5}Mn_{0.5}]O_2$, the obtained spherical precursors were mixed with NaOH (Na : [Ni+Mn] = 1:1 molar ratio), calcined at 750 ^oC for 24 h in oxygen gas, and quenched under vacuum. For the (5 mol)-MgO –NM55 and MgO-$Na[Ni_{0.5}Mn_{0.5}]O_2$ cathodes, $[Ni_{0.5}Mn_{0.5}](OH)_2$ precursor was mixed with MgO nanopowder and NaOH (Na : Mg : [Ni+Mn] = x : (1-x) : 1, x = 0.05, 0.1, molar ratio), and calcined with NaOH following the same calcination process.

Material Characterizations

The particle size distribution was measured using a particle size analyzer (PSA, CILAS 1090). The chemical composition of the prepared powders was determined using inductively coupled plasma spectroscopy (ICP, OPIMA 8300, PerklinElmer). A powder X-ray diffractometer (XRD) spectrometry (Rigaku, Rint-2000) using Cu Kα radiation was employed to identify the crystalline phases of the prepared powders. XRD data were obtained in a 2θ range of 10 to 80° with a step size of 0.03°. The FULLPROF Rietveld program was used to analyze the powder diffraction patterns.[RS1] The morphology of the prepared powders was obtained using scanning electron microscopy (SEM, JSM-6340F, JEOL). Line scanning of the polished surfaces of the as-prepared $Na[Ni_{0.5}Mn_{0.5}]O2$ and MgO-$Na[Ni_{0.5}Mn_{0.5}]O_2$ powders was carried out using an electron probe micro-analyzer (EPMA, JXA-8100, JEOL). Transmission electron microscopy

(TEM, JEM2010, JEOL), and energy dispersive X-ray spectroscopy (EDX, JEM 2100F, JEOL) analyses were also carried out. X-ray photoelectron spectroscopy (XPS, PHI5600, Perkin-Elmer, USA) data were collected in macro mode (3 mm × 3 mm). During the XPS measurements, the samples were first transferred into a hermetically sealed transfer chamber in a glove box and then transferred into the vacuum chamber of the XPS machine to avoid any exposure to the ambient conditions.

Reference

RS1. T. Roisnel, J. Rodriguez-Carvajal, Full Prof Manual, Institute Laue-langevin, 2002, Grenoble, France.

Electrochemical Test

Electrochemical testing was carried out in a 2032 coin-type cell using Na metal (Alfa Aesar, USA) as the anode. Electrodes were fabricated by blending active cathode powders (85 wt%), carbon black (7.5 wt%), and polyvinylidene fluoride (7.5 wt%) in N-Methyl-2-pyrrolidone (Daejung Chem, Korea). The slurry was then cast on aluminum foil (Hohsen Corp., Japan) and dried in a vacuum oven at 110 °C for 12 h. Disks of 14 ϕ were punched out for coin cells. The electrolyte solution was 0.5 M $NaPF_6$ (Tokyo Chemical Industry, Japan) in a 98:2 volumetric mixture of propylene carbonate (Tokyo Chemical Industry Japan) and fluoro ethylene carbonate (Tokyo Chemical Industry, Japan). All cells were prepared in an Ar-filled glove box (MBRAUN, German). The fabricated cathodes and sodium metal anodes were separated by a glass fiber (Advantec, USA) to prevent short circuiting. The loading amount of the active material for all the electrode was 2.5 ~ 3.0 mg cm^{-2} in coin-type half-cell. These half-cells were typically cycled in the constant current mode at a 0.1 C-rate (1 C = 150 mA g^{-1}) within the voltage range of 2.0 - 4.2 V versus Na/Na^+. The anode was fabricated by blending hard carbon as active materials (80 wt%) and polyvinylidene fluoride (20 wt%). The resulting slurry was covered over a copper foil and dried at 110 C for 12 h in a vacuum oven. The full cell balance was achieved by controlling the capacity ratio of the anode to the cathode (N/P ratio) to be 1.2 : 1. Pouch-type (3 × 5 cm) full cells were tested in the voltage range of 1.0-4.1 V.

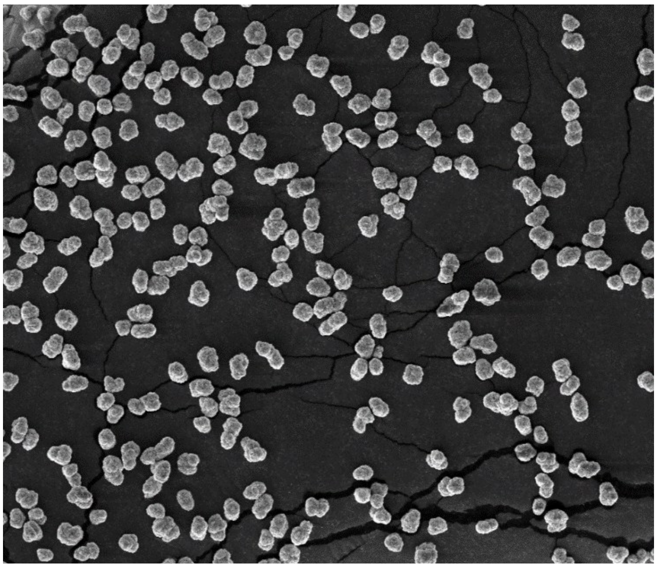

Fig. S1 SEM image $[Ni_{0.5}Mn_{0.5}](OH)_2$ precursor.

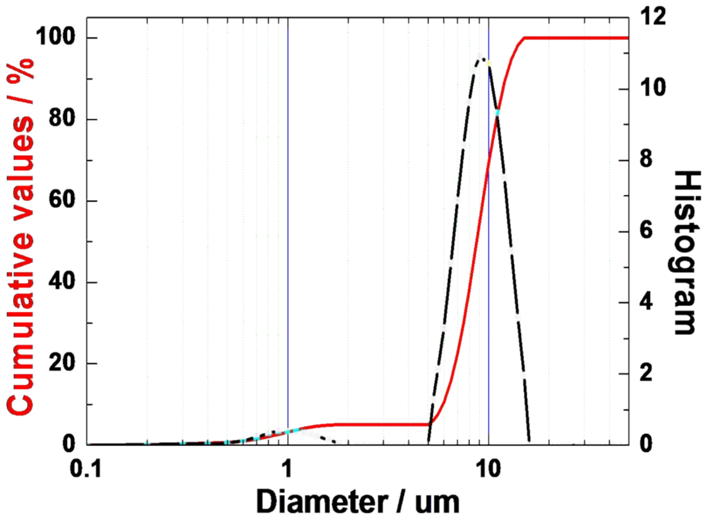

Fig. S2 Particle size analysis (PSA) data of $[Ni_{0.5}Mn_{0.5}](OH)_2$ precursor.

Table S1. Structrual Parameters of NM55 refined by the Rietveld method.

Formula	$Na[Ni_{0.5}Mn_{0.5}]O_2$
Space group	$R\bar{3}m$
Lattice parameters	a_{hex}(Å) = 2.95645(15), c_{hex}(Å) =15.93816 (94)
R_{wp} = 11.6 %	

Atom	site	x	y	z	B (Å^2)	g
Na	3b	0	0	0.5	1.5*	1
Ni	3a	0	0	0	0.389	0.5
Mn	3a	0	0	0	0.389	0.5
O	6c	0	0	0.2644 (1)	0.355	1

*Not refined.

Table S2. Structrual Parameters of MgO-NM55 refined by the Rietveld method.

Formula	$Na[Ni_{0.45}Mg_{0.05}Mn_{0.5}]O_2$
Space group	$R\bar{3}m$
Lattice parameters	a_{hex}(Å) = 2.95954(6), c_{hex}(Å) =15.90443(68)
R_{wp} = 15.5 %	

Atom	site	x	y	z	B (Å^2)	G
Na	3b	0	0	0.5	1.5*	1
Ni	3a	0	0	0	0.364	0.45
Mn	3a	0	0	0	0.364	0.5
Mg	3a	0	0	0	0.364	0.05
O	6c	0	0	0.2601 (2)	0.372	1

*Not refined.

Formula	MgO
Space group	$Fm3m$
Lattice parameters	a_{hex}(Å) = 4.20180(34)
R_{wp} = 15.5 %	

Atom	site	x	y	z	B (Å^2)	g
Mg	4a	0	0	0	0.5	1
O	4c	0.5	0.5	0.5	0.5	1

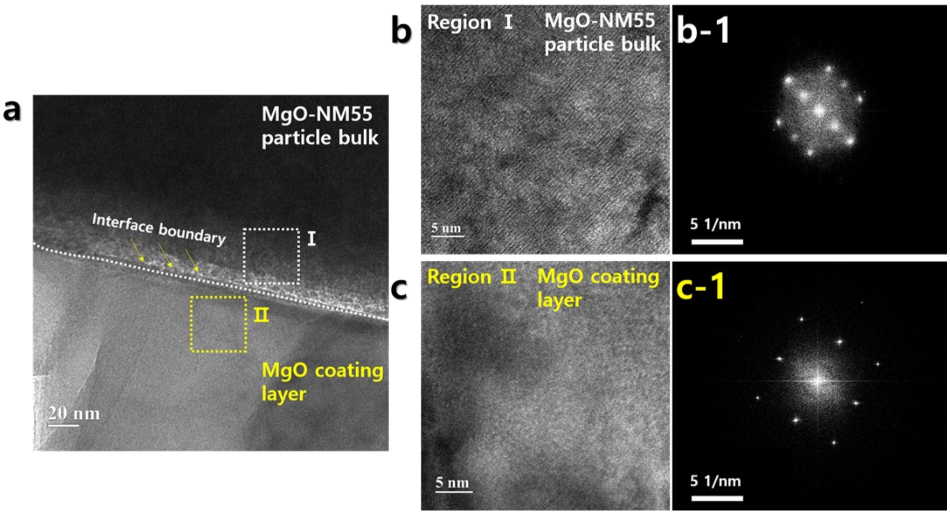

Fig. S3 (a) TEM image of MgO-NM55 particle surface. (b) HR-TEM image and (b-1) FFT pattern for bulk region (white square region, marked as “ Ⅰ “ in (a)) of MgO-NM55 particle. (c) HR-TEM image and (c-1) pattern for MgO cotaing layer region (yellow square region, marked as “Ⅱ“ in (a) of MgO-NM55 particle.

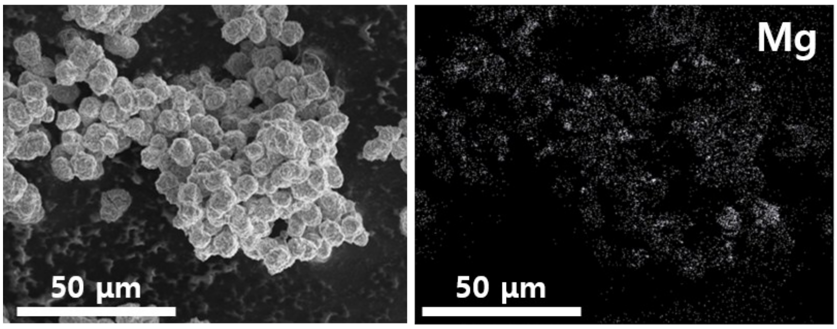

Fig. S4 Low magnification SEM image and corresponding EDX mapping of as-prepared MgO-NM55.

Table S3. ICP-AES results of $[Ni_{0.5}Mn_{0.5}](OH)_2$ precursor and the NM55 and MgO-NM55 cathodes.

	Metal stoichiometry determined by ICP-AES			
	Na	Ni	Mn	Mg
$[Ni_{0.5}Mn_{0.5}](OH)_2$		0.4983	0.5017	
NM55	97.63	0.4952	0.5048	
MgO-NM55	98.89	0.4507	0.4545	0.0948

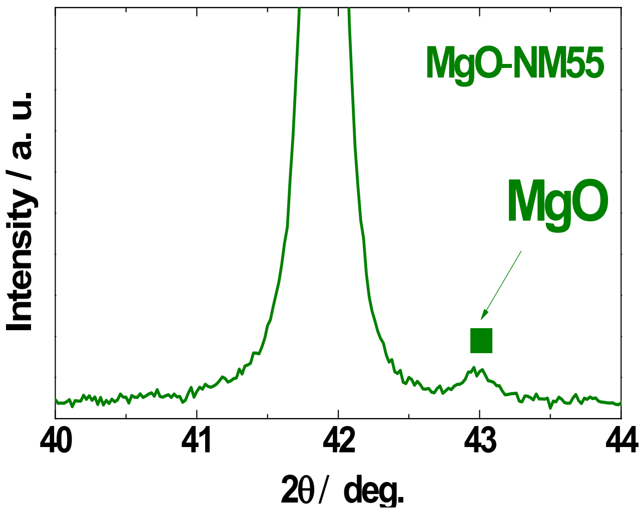

Fig. S5 XRD pattern of the MgO-NM55 cathode. The minor MgO cubic phase is marked with a square.

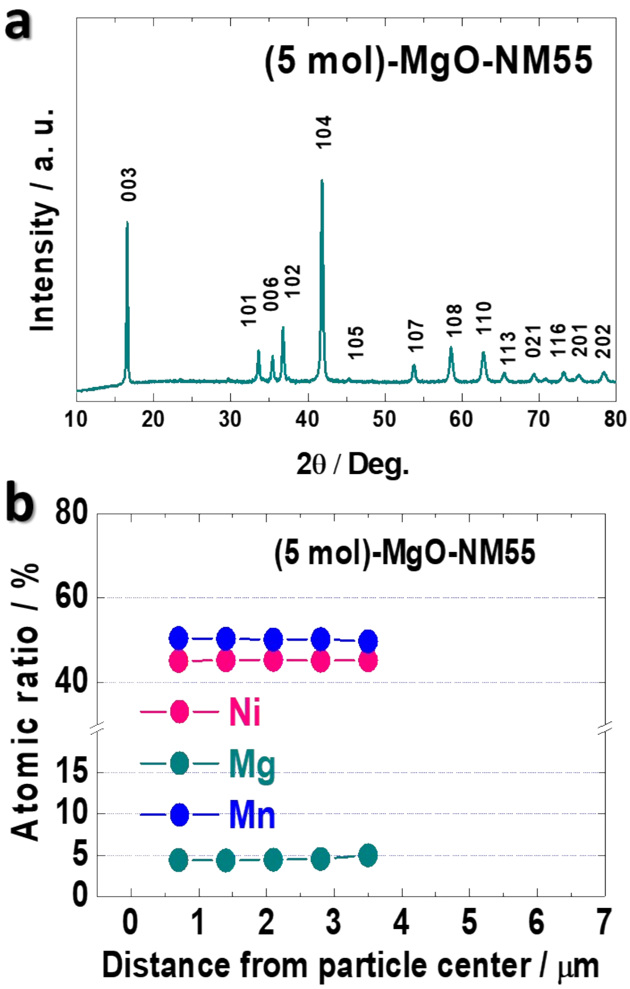

Fig. S6 (a) XRD pattern and (b) EPMA data of the (5mol)-MgO-NM55 cathode.

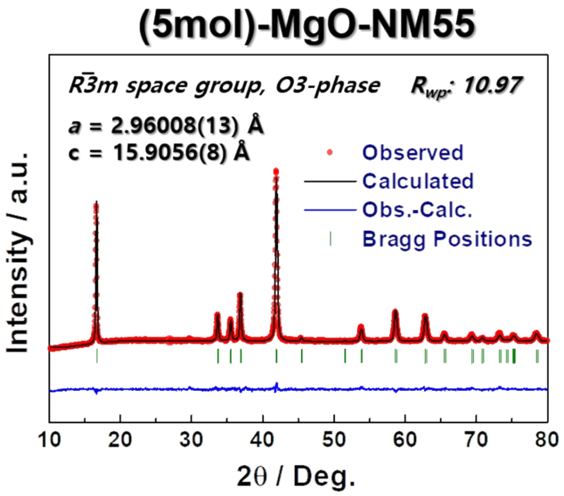

Fig. S7 Rietveld refined XRD pattern of (5mol)-MgO-NM55.

Table S4. Structrual Parameters of (5mol)-MgO-NM55 refined by the Rietveld method.

Formula Space group Lattice parameters R_{wp} = 10.97 %					$Na[Ni_{0.45}Mg_{0.05}Mn_{0.5}]O_2$ $R\bar{3}m$ a_{hex}(Å) = 2.96008(13), c_{hex}(Å) =15.9056(8)	
Atom	site	x	y	z	B (Å^2)	G
Na	3b	0	0	0.5	1.5*	1
Ni	3a	0	0	0	0.362	0.45
Mn	3a	0	0	0	0.362	0.5
Mg	3a	0	0	0	0.362	0.05
O	6c	0	0	0.2609 (1)	0.306	1

*Not refined.

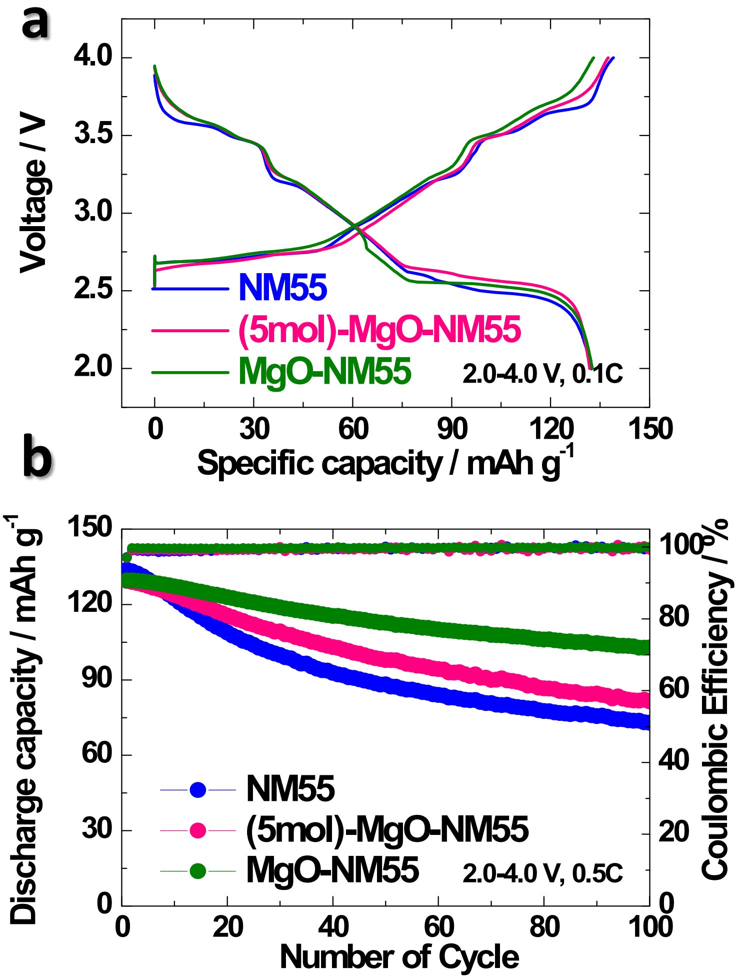

Fig. S8 (a) Initial charge-discharge voltage curves at a 0.1 C-rate (15 mA g^{-1}) and (b) cycle life test of the NM55, (5mol) MgO-NM55, and MgO-NM55 cathodes at a 0.5 C-rate (75 mA g^{-1}) in the voltage range of 2.0-4.0 V.

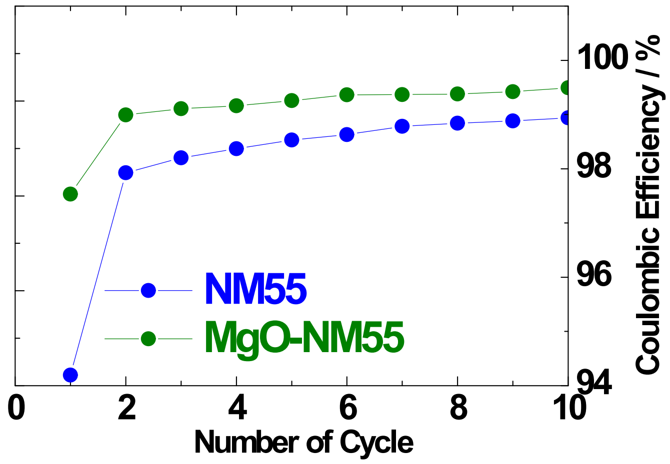

Fig. S9 Coulombic efficiency of NM55 and MgO-NM55 cathodes at a 0.5 C-rate (75 mA g^{-1}) in the voltage range of 2.0-4.0 V.

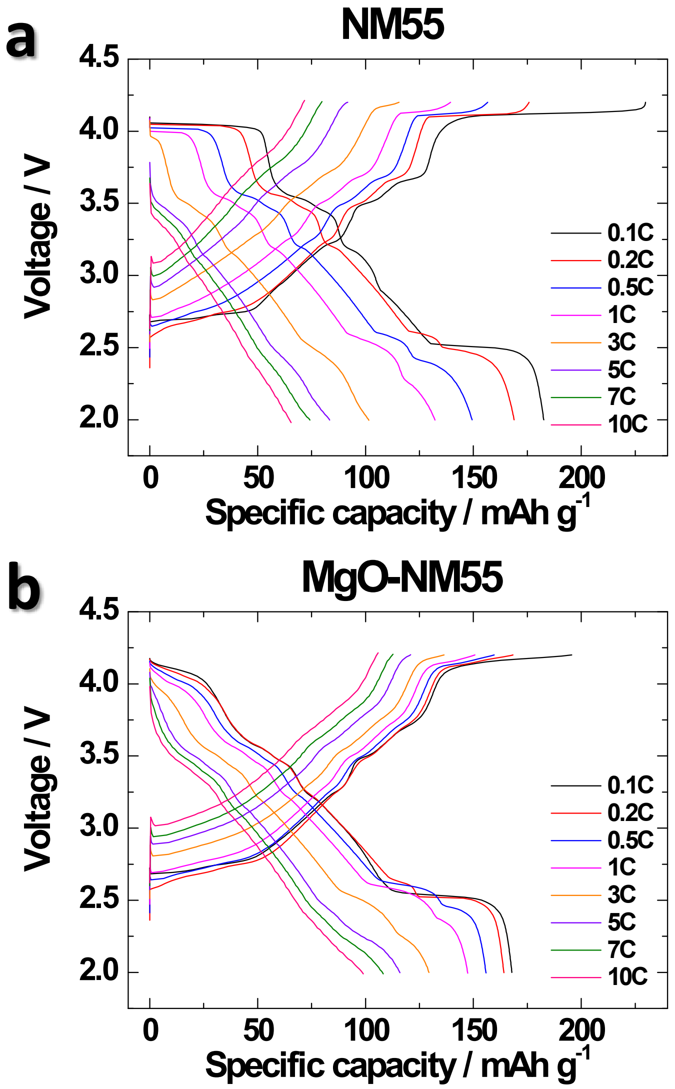

Fig. S10 Charge-discharge curves of the NM55 and MgO-NM55 cathodes at different C-rates (0.1 C to 10 C) in the voltage range of 2.0-4.2 V.

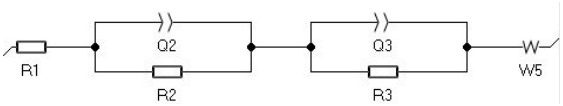

Fig. S11 Fitting circuit diagram for EIS analysis.

Table S5. The R_{sf} and R_{ct} values for the HC/NM55 and HC/MgO-NM55 full cell at 30th cycle.

Sample	1st R_{sf} (Ω)	1st R_{ct} (Ω)	30th R_{sf} (Ω)	30th R_{ct} (Ω)
HC/NM55	1.7	5.96	1.89	25.9
HC/MgO-NM55	0.37	2.36	0.45	3.53

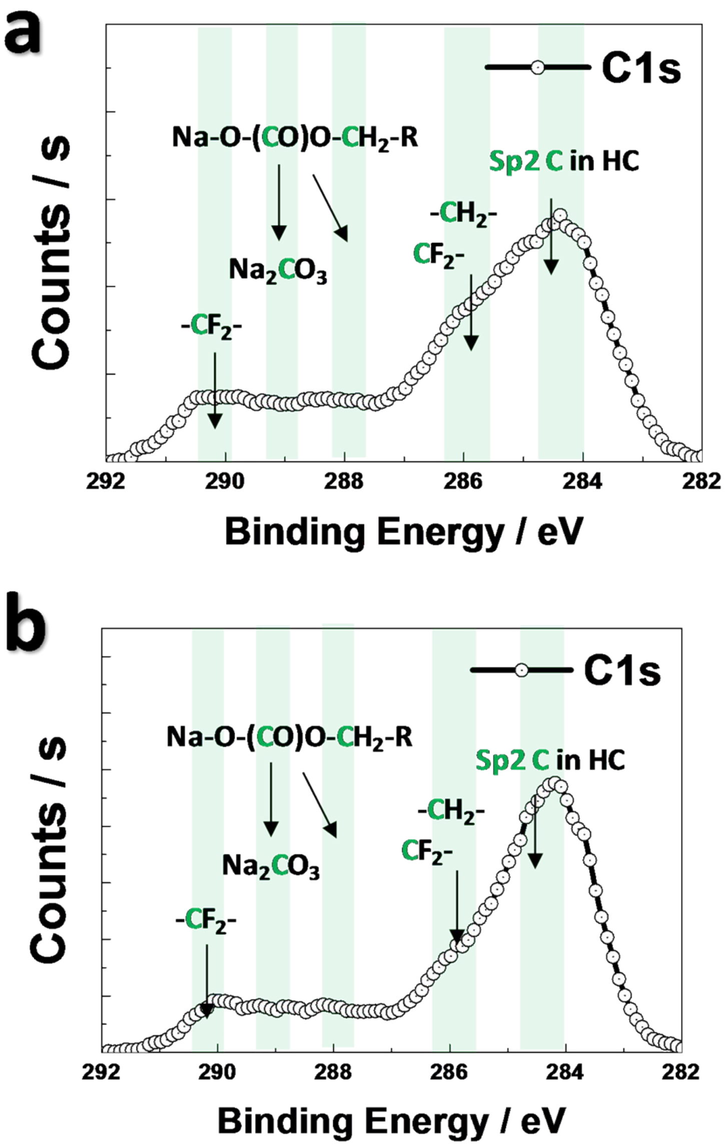

Fig. S12 C1s spectra from XPS results for the cycled (a) NM55 and (b) MgO-NM55 cathodes collected from the pouch-type full cell after 200 cycles.

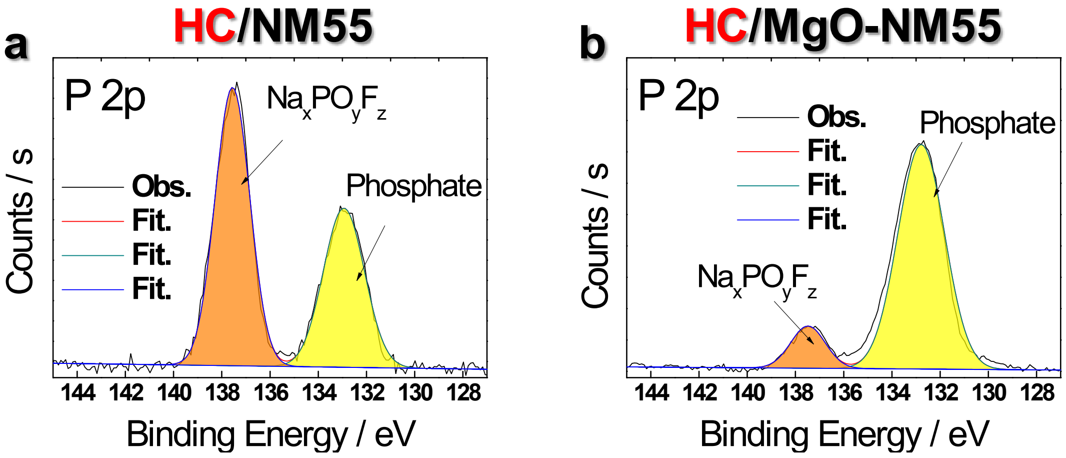

Fig. S13 XPS spectra of P 2p for cycled hard carbon anodes: (a) NM55/HC full cell and (b) MgO-NM55/HC full cell after 200 cycles (Obs.:observed, Fit.: fitted).

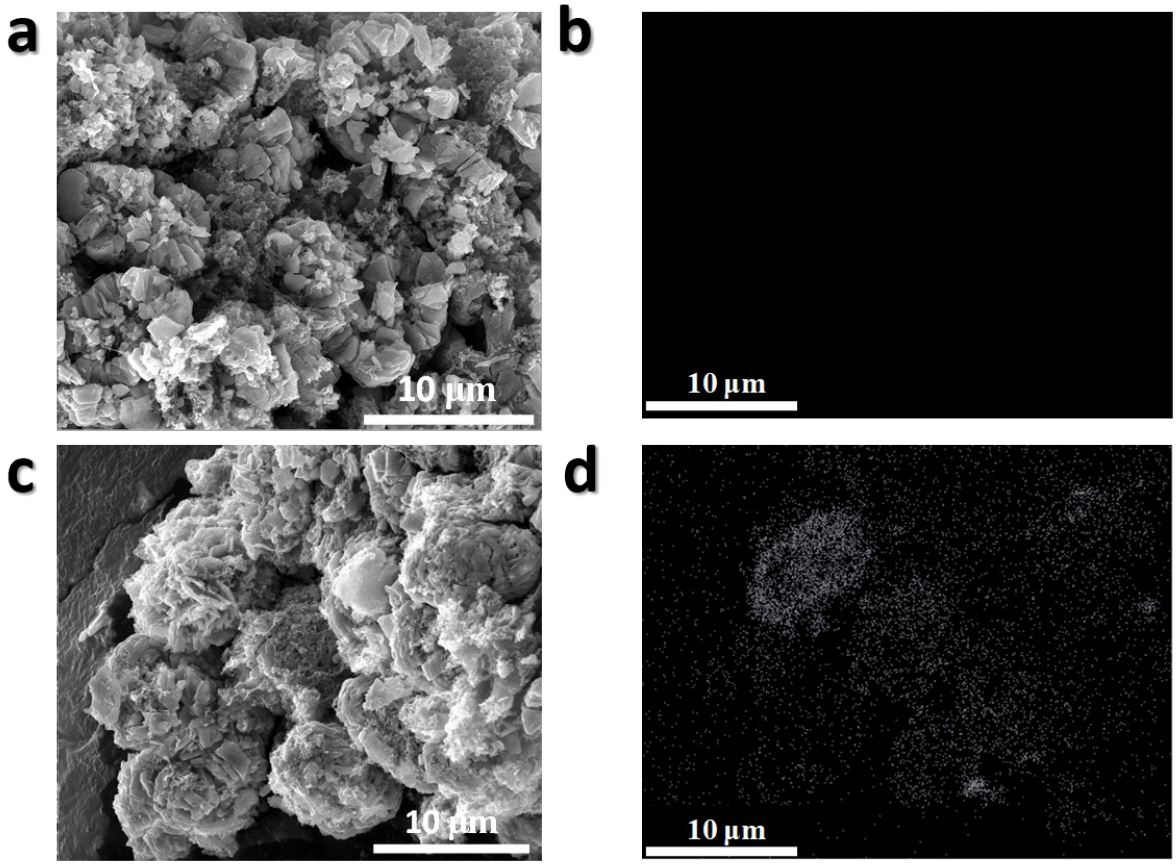

Fig. S14 SEM images and corresponding EDX mapping (Mg element) data for the cycled (a-b) NM55 and (c-d) MgO-NM55 cathodes collected from the pouch-type full cell after 200 cycles.

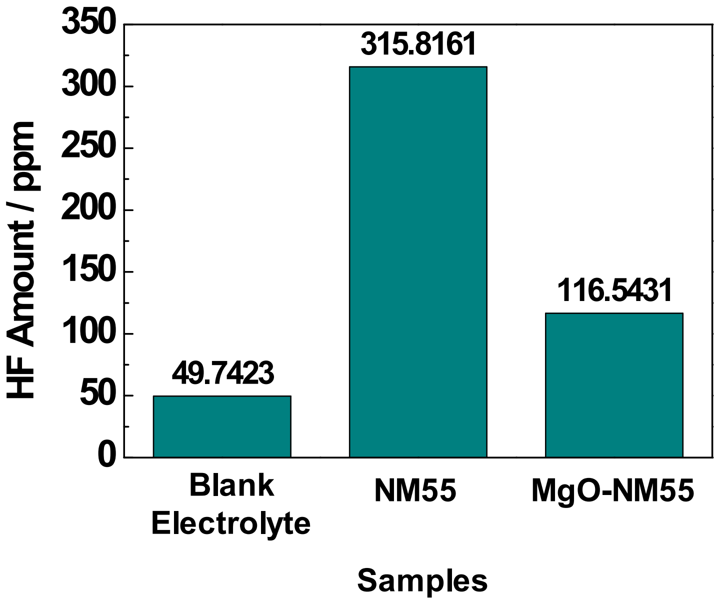

Fig. S15 HF titration results of the pouch-type NM55/HC and HC/MgO-NM55 full cell after 200 cycles.

Table S6. Comparisons table comparing the performance of the cathode material to similar materials.

Cathode	Cut-off Potential	1st Discharge Capacity	Best Cycling Performance	Best Rate Performance	Full Cell	Ref
NaFe$_x$(Ni$_{0.5}$Mn$_{0.5}$)$_{1-x}$O$_2$	2.0-4.0 V	130 mAh g^{-1} at 12 mA g^{-1}	96.4% 30th at 12 mA g^{-1}	86 mAh g^{-1} at 2.4 A g^{-1} (2.0-4.0V)	X	S1
NaNi$_{0.5}$Mn$_{0.5}$O$_2$	2.2-3.8 V	125 mAh g^{-1} at 8 mA g^{-1}	72% 50th at 48 mA g^{-1} 70% 50th at 240 mA g^{-1}	105 mAh g^{-1} at 240 mA g^{-1} (2.0-4.0V)	X	S2
NaNi$_{0.5}$Mn$_{0.5}$O$_2$	2.0-4.0 V	141 mAh g^{-1} at 12 mA g^{-1}	90% 100th at 12 mA g^{-1}	80 mAh g^{-1} at 480 mA g^{-1} (2.0-4.0V)	X	S3
NaNi$_{0.5}$Mn$_{0.5-x}$Ti$_x$O$_2$	2.0-4.0 V	134 mAh g^{-1} (2.0-4.0) at 12 mA g^{-1}	85% 200th at 240 mA g^{-1} (2.0-4.0)	95 mAh g^{-1} at 1.2 A g^{-1} (2.0-4.0V)	X	S4
	2.0-4.2 V	140 mAh g^{-1} (2.0-4.2) at 12 mA g-1	78% 200th at 240 mA g^{-1} (2.0-4.2)			
NaNi$_{0.45}$Cu$_{0.05}$Mn$_{0.4}$Ti$_{0.1}$O$_2$	2.0-4.0 V	124 mAh g^{-1} at 24 mA g^{-1}	70.2% 500th at 240 mA g^{-1}	81 mAh g^{-1} at 2.4 A g^{-1} (2.0-4.0V)	X	S5
Carbon/NaNi$_{0.5}$Mn$_{0.5}$O$_2$	1.2-3.6 V	240 mAh g$^{-1}_{(C)}$ at 25 mA g$^{-1}_{(C)}$	75% 45th at 25 mA g$^{-1}_{(C)}$ 58% 80th at 300 mA g$^{-1}_{(C)}$	-	O (Coin)	S6
NaNi$_{0.5}$Mn$_{0.5}$O$_2$	2.2-3.8 V	130 mAh g^{-1} at 23.9 mA g^{-1}	62% 50th at 23.9 mA g^{-1}	-	X	S7
NaNi$_{0.5}$Mn$_{0.5}$O$_2$	2.0-4.0 V	147 mAh g-1 (2.0-4.0) at 12 mA g^{-1}	74% 50th at 60 mA g^{-1} (2.0-4.0 V)	96 mAh g^{-1} at 1.2 A g^{-1} (2.0-4.0V)	O (Coin)	S8
	2.0-4.2 V	220 mAh g-1 (2.0-4.2) at 12 mA g^{-1}	58% 50th at 60 mA g^{-1} (2.0-4.2 V)			
NaNi$_{0.5}$Mn$_{0.5}$O$_2$	2.1-4.0 V	137 mAh g^{-1} at 12 mA g^{-1}	82% 75th at 12 mA g^{-1}	92 mAh g^{-1} at 120 mA g^{-1} (2.0-4.0V)	X	S9
MgO-NaNi$_{0.5}$Mn$_{0.5}$O$_2$ (Tap density: 2.0 g cm^{-3})	**2.0-4.0 V**	**132.6 mAh g^{-1} at 15 mA g^{-1}**	**80 % 100th at 75 mA g^{-1}**	**100.2 mAh g^{-1} at 1.5 A g^{-1} (2.0-4.2 V)**	**O (Pouch)**	**This work**
	2.0-4.2 V	**167 mAh g^{-1} 15 mA g^{-1}**	**75 % 100th at 75 mA g^{-1}**			

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