Supporting Information

Unlocking Synergistic Effects of Gradient Engineering, Mg Doping, and In-Situ Li Conductive Coating for High-performances Ni-rich LiNi_{0.92}Co_{0.04}Mn_{0.04}O₂ Cathode Materials

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S1. Experimental

S1.1 Preparation of Pristine CG-NCM92 and MP-*x*@CG-NCM92 Cathode materials

A concentration-gradient $Ni_{0.92}Co_{0.04}Mn_{0.04}(OH)_2$ hydroxide was prepared by introducing a thoroughly mixed solution of 2 M NiSO₄·6H₂O and 2 M CoSO₄·7H₂O into a Taylor-Vortex Reactor (TVR). Simultaneously, solutions of 7.2 M ammonium hydroxide and 4 M sodium hydroxide were added to regulate the pH, where the ammonium hydroxide served as a chelating agent and the sodium hydroxide functioned as a precipitant. The reaction was conducted under controlled conditions at 60 °C, with the pH maintained at 11.2 and continuous stirring at 600 rpm. After 12 h, a 2 M MnSO₄·H₂O solution was introduced at the midpoint of the reactor. The precipitated hydroxide was then extensively washed with deionized water and ethanol, filtered, and dried overnight at 60 °C.

Subsequently, the obtained hydroxide was mixed with LiOH·H₂O in a molar ratio of 1:1.04 using dry ball milling for 2 h. This mixture was then calcined at 745 °C for 20 h in a pure oxygen environment, yielding concentration-gradient Ni_{0.92}Co_{0.04}Mn_{0.04}(OH)₂ (Pristine CG-NCM92) hydroxide powders. To produce the designated MP-x@CG-LiNi_{0.92}Co_{0.04}Mn_{0.04}O₂, the CG-NCM92 hydroxide powders were further blended with LiOH·H₂O and varying amounts of magnesium phosphate (MgHPO₄, 99% purity, Sigma Aldrich) and then calcined under the same conditions. The magnesium phosphate content was varied at 0.01, 0.02, and 0.03 mol%, corresponding to the samples labeled as MP-1@CG-NCM92, MP-2@CG-NCM92, and MP-3@CG-NCM92, respectively (Fig. S1).

S1.2 Materials Characterizations

X-ray diffraction (XRD) analysis was conducted using a Bruker D2 PHASER (Cu Ka radiation, $\lambda = 0.1534753$ nm, 30 kV, 10 mA, Germany) to examine the structural properties, phase composition, and crystallinity of pristine CG-NCM92 and MP-x@CG-NCM92 samples, including both fresh electrodes and cycled electrode (at 1C/1C in the voltage range of 2.8-4.3 V for 300 cycles). Rietveld refinements were performed using TOPAS software (v 4.2). The morphological features, microstructures, and elemental distributions of pristine CG-NCM92 and MP-x@CG-NCM92 were analyzed via scanning electron microscopy and transmission electron microscopy combined with energy-dispersive spectroscopy (Hitachi, Japan). The particle size distributions were evaluated through a particle size analyzer (LS 13 320, Beckman Coulter, USA). The crystal structure and phase transitions of pristine CG-NCM92 and MP-x@CG-NCM92, in both powder form and electrode form, were comprehensively analyzed before and after prolonged cycling (1C/1C for 300 cycles) using high-resolution transmission electron microscopy combined with selected area electron diffraction (HR-TEM/SAED, JEOL JEM-2100F, Japan). Additionally, A Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS V, Argon cluster sputtering source, ION-TOF GmbH, Germany) instrument, featuring an O₂ analysis beam and Cs⁺ sputtering beams, was employed to examine the surface properties of the cycled CG-NCM92 cathodes. X-ray photoelectron spectroscopy (XPS, PHI5600, PerkinElmer, USA) was employed to analyze the surface elemental composition and oxidation states of the synthesized powders before and after extended cycling tests, with the acquired spectra processed using XPSPEAK 4.1 software. Inoperando X-ray measurements were performed using an EMPYREAN III Malvern Panalytical Xray diffractometer during the charge-discharge process of a pouch cell (dimensions: 3×5 cm²). A current of 0.1C was applied within a voltage range of 2.7-4.2 V to monitor real-time structural

changes occurring during the lithium-ion intercalation and deintercalation process. The chemical compositions of pristine CG-NCM92 and MP-*x*@CG-NCM92 cathode materials were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7900, Agilent Technologies, USA).

S1.3 Cell Fabrication

Electrochemical performance was assessed using CR2032-type coin cells. The positive electrode was fabricated through a slurry-casting method, where pristine CG-NCM92 and MP@CG-NCM92 powders were combined with Super-P and polyvinylidene fluoride (PVDF) in an 80:10:10 weight ratio. This mixture was uniformly dispersed in N-methyl pyrrolidone (NMP), coated onto aluminum foil, and dried at 60 °C for 12 h. The active material mass loading was maintained at 2–3 mg cm⁻². The CR2032-type coin half-cells were assembled inside an argon-filled glove box, using lithium metal as the anode, a microporous polyethylene (PE) membrane (Celgard 2400, USA) as the separator, and an electrolyte composed of 1 M LiPF₆ dissolved in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (Aldrich).

S1.4 Electrochemical Performance Measurements

Charge and discharge tests were conducted at various C-rates ($1C = 200 \text{ mA g}^{-1}$) within a voltage range of 2.8–4.3 V (*vs.* Li/Li⁺) at both room temperature (RT) and 45 °C using a BCS-805 workstation (Bio-Logic, France). Cyclic voltammetry (CV) measurements were performed using an Autolab electrochemical workstation (PGSTAT302N, the Netherlands) at a scan rate of 0.01 mV s⁻¹ within a voltage range of 2.8–4.5 V (*vs.* Li/Li⁺). Electrochemical impedance spectroscopy (EIS) was carried out on the same workstation over a frequency range of 1 MHz to 0.01 Hz with an amplitude of 5 mV. The galvanostatic intermittent titration technique (GITT) was applied by

performing charge and discharge cycles at a constant current of 0.1C for 10 min, followed by a 40min relaxation period within the voltage range of 2.8–4.3 V at RT. Operando microcalorimetry analysis was conducted using an MMC274 Nexus® system (Netsch, Germany) to quantify the heat generated during charge and discharge processes. Additionally, endothermic and exothermic reactions, along with the electrochemical performance of CR2032-type coin cells, were simultaneously analyzed at 3C/3C within a voltage range of 2.8–4.3 V (*vs.* Li/Li⁺) under isothermal conditions at 35 °C, with a controlled heating rate of 0.5 °C min⁻¹.

S1.5 Post-mortem Analysis

The electrode morphology and particle cross-sections, both before and after cycling, were examined using cross-sectional polisher scanning electron microscopy (SEM, Hitachi S-2600H, Japan) and a focused ion beam Microscope (FIB-FESEM, FEI Helios G4 UX), respectively. High-resolution transmission electron microscopy (HR-TEM), Selected Area Electron Diffraction (SAED) of pristine CG-NCM92 and MP-2@CG-NCM92 electrodes, following long-term cycling (at 1C/1C for 300 cycles), were conducted using a JEOL JEM-2100F high-resolution transmission electron microscope (Japan).

S1.6 Theoretical Calculation

Electrostatic analyses and density functional theory (DFT) were performed to determine the arrangement of transition metals (TMs) in Ni-rich LiNi_{0.92}Co_{0.04}Mn_{0.04}O₂ (NCM92) and Mgdoped NCM92. A $4 \times 4 \times 1$ supercell of pristine NCM92 was built with 48 Li, 44 Ni, 2 Co, and 2 Mn atoms (Li₄₈Ni₄₄Co₂Mn₂O₉₆). Two Mg-doped NCM92 models were constructed: one has 1 Mg substituting 1 Li site in the Li layer, referred to as Mg_{Li}NCM92 ([Li₄₇Mg₁]Ni₄₄Co₂Mn₂O₉₆), and the other has 1 Mg substituting 1 Ni site in the TM layer, named $Mg_{Ni}NCM92$ ($Li_{48}[Ni_{43}Mg_1]Co_2Mn_2O_{96}$).

Spin-polarized DFT calculations were performed using the Projector Augmented-Wave (PAW) [1] pseudopotential method implemented in the Vienna Ab initio Simulation Package (VASP) code [2]. The Perdew–Burke–Ernzerhof (PBE) [3] functional was employed to approximate the exchange–correlation (XC) energy for all DFT calculations of atomistic structures. Heyd-Scuseria-Ernzerhof (HSE) functional [3] was used for electronic structures including spin density difference (SDD), number of unpaired spin electrons (NUS) and Bader charge analysis. A $2 \times 2 \times 1$ k-point mesh was applied to all structures. The grain boundary (GB) calculations were performed for GB (Σ 3[110]/(1 1 02)) with 192 atoms. The GB was modelled by a $2 \times 2 \times 1$ k-point mesh. An energy cutoff of 600 eV as well as an energy and force convergence criterion of 10⁻⁴ eV Å⁻¹ was used for all calculations. The atomic structures were visualized using VESTA [4].



Fig. S1. Schematic diagram of in-situ Mg²⁺-doping and Li₃PO₄-coating on MP-*x*@CG-NCM92 synthesis steps.



Fig. S2. XRD Rietveld refinement results of (a) Pristine CG-NCM92, (b) MP-1@CG-NCM92, (c) MP-2@CG-NCM92, and (d) MP-3@CG-NCM92 layered oxides materials, respectively.



Fig. S3. The EDS mapping of (a) Pristine CG-NCM92, (b) MP-1@CG-NCM92, (c) MP-2@CG-NCM92, and (d) MP-3@CG-NCM92, respectively



Fig. S4. (a) FE-SEM cross-sectional image of MP-2@CG-NCM92 particle, (b) EDS line scanning profiles of Ni, Co, Mn, Mg, and P elements of MP-2@CG-NCM92 particle,



Fig. S5. Particle size distribution of pristine CG-NCM92 (black line) and MP-2@CG-NCM92 (red line) powder samples, respectively.



Fig. S6. The FFT and IFFT images of (a) Pristine CG-NCM92 and (b) MP-2@CG-NCM92 cathode materials, respectively.



Fig. S7. The HR-TEM images of (a) MP-2@CG-NCM92, and (b) MP-3@CG-NCM92, respectively



Fig. S8 XPS spectra of pristine CG-NCM92 and MP-2@CG-NCM92 layered oxide powders were analyzed for the following elements: (a). Ni 2p, (b). O 1s, (c). C 1s, (d). P 2p, and (e, f) Mg 1s, respectively.



Fig. S9. TOF-SIMS depth profiles and corresponding three-dimensional (3D) images showing the spatial distribution of selected ion fragments in MP-2@CG-NCM92 cathode powder: (a) Ni⁺, (b) Co⁺, (c) Mn⁺, and (d) Mg⁺.



Fig. S10. The TEM image and the corresponding EDS maps of Ni, Co. Mn, and Mg elements in MP-2@CG-NCM92



Fig. S11. XPS spectra of pristine CG-NCM92 and MP-2@CG-NCM92 layered oxide powders were analyzed for the following elements at 0 min etched time: (a) Mn 2p, (b) Co 2p, and (c). Li 1s, respectively.

XPS profiles of Li 1s, O 1s, and C 1s are provided to investigate the surface residual species on pristine CG-NCM92 and MP-2@CG-NCM92 oxide samples (Figs. S8 and S11). The Li 1s spectra of both samples, shown in Fig. S11(c), display two distinct peaks corresponding to intercalated lithium (Li_{intercalated}) and surface lithium (Li_{surface}). The areal percentage of surface lithium in pristine CG-NCM92 (55%) is higher than that in MP-2@CG-NCM92 (39%), likely due to a greater presence of residual lithium compounds on the surface of pristine CG-NCM92. The XPS spectra of O 1s and C 1s spectra provides further evidence for the observed differences in surface chemistry between pristine CG-NCM92 and MP-2@CG-NCM92. As shown in Fig S8(b), the O 1s spectra reveal two prominent peaks: one at approximately ~529 eV, corresponding to lattice oxygen (TM-O) [5,6], and another near 532 eV, associated with surface oxygen impurities (O_{impurity}) [7,8]. These oxygen impurities likely arise from active oxygen species (e.g., O⁻, O²⁻, or CO_3^{2-}) associated with impurity compounds on the particle surface [9,10]. The areal percentage of the O_{impurity} in MP-2@CG-NCM92 is around 29%, which is significantly lower than the 38% observed in pristine CG-NCM92. This indicates that impurity compounds, such as Li₂CO₃ and LiOH are effectively reduced on the surface of MP-2@CG-NCM92. Additionally, the C1s spectra, illustrated in Fig. S8(c) [11], display two main peaks attributed to CO_3^{2-} and C - C species [10,12]. The area percentage of the CO₃²⁻ species is lower in MP-2@CG-NCM92 (13%) compared to pristine CG-NCM92 (16%), further confirming the reduced presence of surface impurities in MP-2@CG-NCM92. The improved surface stability of MP-2@CG-NCM92 can be attributed to several factors. The magnesium-oxygen bond is stronger than the nickel-oxygen bond and the lithium-oxygen bond, enhancing the stability of the lattice oxygen structure [13,14]. Additionally, the formation of a Li₃PO₄ coating layer, which exhibits relatively good ionic conductivity and stability in air, helps reduce lithium residues and minimize the content of residual lithium salts (Li₂CO₃ and LiOH), thereby further suppressing the formation of byproducts [15-17].



Fig. S12. Atomic structures of (a) pristine NCM92, (b) Mg-doped NCM92 with Mg substitution at the Li site (Mg_{Li}NCM92) and (c) Mg-doped NCM92 with Mg substitution at the Ni site (Mg_{Ni}NCM92).



Fig. S13. Bader charge analysis of (a) pristine NCM92, (b) Mg_{Li}NCM92 and (c) Mg_{Ni}NCM92.



Fig. S14. Side view of grain boundary ($\Sigma 3[110]/(102)$) of Mg-doped LiNiO₂ with (a) Mg substitution at the Li site and (b) Mg substitution at the Ni site.



Fig. S15. The dQ/dV curves of (a) Pristine CG-NCM92, (b) MP-1@CG-NCM92, (c) MP-2@CG-NCM92, and (d) MP-3@CG-NCM92, respectively, at 1C/1C for 100 cycles.



Fig. S16. DC polarization (I-V) curves of pristine CG-NCM92 and MP-2@CG-NCM92 electrodes.



Fig. S17. Operando micro-calorimetry measurements were performed on CR2032 coin cells with (a) Pristine CG-NCM92 and (b) MP-2@CG-NCM92 electrodes, respectively, the tests were conducted at 3C/3C within a voltage range of 2.8–4.3 V (vs. Li/Li⁺) under temperature of 35 °C, with a heating rate of 0.5°C per min.

Fig. S18. Self-discharge characteristics of pristine CG-NCM92 and MP-2@CG-NCM92: (a) Voltage-time profile, (b) Specific capacity retention as a function of time, (c) Discharge curves after a 14-day rest, and (d) AC impedance after self-discharge test.

Fig. S19. (a) XRD patterns and (b) corresponding magnified views of pristine CG-NCM92 and MP-2@CG-NCM92 electrodes before cycling and after 300 cycles at 1C/1C within a voltage range of 2.8–4.3 V at room temperature.

Fig. S20. SEM images of (a) pristine CG-NCM92 and (b) MP-2@CG-NCM92 electrodes after 300 cycles at a 1C/1C- rate within the voltage range of 2.8–4.3 V at RT.

Fig. S21. Cross-sectional polisher SEM images of (a) Pristine CG-NCM92 and (b) MP-2@CG-NCM92-based electrodes after 300 cycles at 1C/1C in the voltage range of 2.8-4.3V at room temperature.

Fig. S22. FIB FE-SEM images of (a) Pristine CG-NCM92 and (b) MP-2@CG-NCM92 electrodes after 300 cycles at a 1C/1C- rate within the voltage range of 2.8–4.3 V at room temperature.

Fig. S23. XPS spectra of cycled pristine CG-NCM92 and MP-2@CG-NCM92 electrodes after 300 cycles at 1C/1C within a voltage range of 2.8–4.3 V at room temperature: (a) F 1s, (b) C 1s, and (c) O 1s, respectively.

Fig. S24. TOF-SIMS depth profiles of selected chemical species in pristine CG-NCM92 and MP-2@CG-NCM92 cathodes, including CH₂O⁻, LiF₂⁻, F⁻, HPO₃F⁻, and Li₂O⁺, respectively.

Fig. S25.Three-dimensional (3D) images of TOF-SIMS fragment distributions of selected chemical species in pristine CG-NCM92 and MP-2@CG-NCM92 cathodes, including CH₂O⁻, LiF₂⁻, F⁻, HPO₃F⁻, and Li₂O⁺, respectively.

Sample	Pristine CG-NCM92	MP-1@CG- NCM92	MP-2@CG- NCM92	MP-3@CG- NCM92
a (A)	a (A) 2.869 2		2.875	2.879
c (A)	14.177	14.191	14.214	14.252
V (A ³)	101.083	101.346	101.773	102.358
c/a	4.941	4.942	4.944	4.949
FWHM of (003)	0.1565	0.1659	0.1679	0.1834
$\mathbf{R} = \mathbf{I}_{(003)} / \mathbf{I}_{(104)}$	1.83	1.72	1.69	1.66
Crystallite size on (003) (nm)	51.5	48.5	47.9	43.9
$\mathbf{R}_{\mathrm{wp}}{}^{d}$ (%)	2.39	2.23	2.5	2.35
GoF ^e	1.27	1.18	1.31	1.22

Table S1. Rietveld refinement results of pristine CG-NCM92, MP-1@CG-NCM92, MP-2@CG-NCM92, and MP-3@CG-NCM92 layered oxides cathode materials

Sample	Li	Mn	Со	Ni	Mg		
Pristine CG-NCM92							
Chemical Composition obtained by ICP- MS	6.6 ± 0.04 (wt%)	2 ± 0.002 (wt%)	2.16 ± 0.00 5 (wt%)	43.7 ± 0.001 (wt%)	ND		
Normalized Chemical Composition (at%)	1.15 ± 0.00 8	0.04 ± 0.002	$0.04 \pm 0.00 \\ 5$	0.92 ± 0.001	ND		
MP-2@CG-NCM92							
Chemical Composition obtained by ICP- MS	6.4 ± 0.08 (wt%)	1.9 ± 0.03 (wt%)	2.16 ± 0.00 5 (wt%)	43.7 ± 0.001 (wt%)	3928 ± 0.001 (ppm)		
Normalized Chemical Composition (at%)	1.13 ± 0.00 7	0.04 ± 0.002	0.04 ± 0.00 5	0.92 ± 0.001	0.019 ± 0.000 9		
Method detection limit (ppm)	0.0001	0.012	0.001	0.006	0.001		

 Table S2. Chemical composition of pristine CG-NCM92 and MP-2@CG-NCM92 cathode materials measured by ICP-MS.

Structures	a (Å)	c (Å)	<i>V</i> (Å ³)
NCM92	2.947	14.169	120.654
Mg _{Li} NCM92	2.948	14.173	120.889
Mg _{Ni} NCM92	2.947	14.179	120.761

Table S3. Lattice parameters a, c and volume (V) for NCM92 and Mg-doped NCM92(Mg_{Li}NCM92 and Mg_{Ni}NCM92) based on DFT Simulation.

Structures						
NCM92 Mg _{Li} NCM92 Mg _{Ni} NCM92						
Ni		Ni		Ni		
0.856	0.857	1.669	0.858	0.855	0.856	
0.856	0.856	0.848	0.837	0.854	0.857	
0.856	0.86	0.864	0.856	0.854	0.857	
0.856	0.858	0.879	0.858	0.856	0.857	
0.858	0.856	0.859	0.846	0.857	0.857	
0.857	1.681	0.857	0.856	0.857	-	
0.857	Со	0.86	Со	0.857	Со	
0.857	-0.044	0.858	-0.039	0.857	-0.038	
0.871	1.06	0.888	-0.039	0.885	-0.038	
0.889	Mn	0.885	Mn	0.885	Mn	
0.883	2.972	0.886	2.974	0.895	2.973	
0.881	2.973	0.887	2.974	0.895	2.973	
0.857		0.861	Mg	0.856	Mg	
0.855		0.869	0.009	0.854	0.003	
0.856		0.854		0.854		
0.857		0.86		0.855		
0.855		0.862		0.867		
0.873		0.86		0.861		
1.681		0.861		0.867		
0.859		0.861		0.86		
0.858		0.867		0.858		
0.857		0.866		0.857		
0.858		0.854		0.857		
0.859		0.853		0.858		
0.857		0.858		0.856		
0.856		0.859		0.855		
0.857		0.857		0.856		
0.857		0.856		0.856		
0.886		0.873		0.863		
1.679		1.68		1.679		
0.875		1.681		0.866		
0.856		0.873		0.856		
0.858		0.857		0.856		
0.856		0.859		0.855		
0.857		0.839		0.857		
0.859		0.857		0.858		
0.858		0.857		0.857		
0.858		0.859		0.857		

Table S4. Calculated the number of unpaired spin electrons (NUS) of Ni, Co, Mn, and Mg cationsfor NCM92 and Mg-doped NCM92.

	RM	$E_{\rm c}({\rm eV})$
(1)	$3 \text{ Ni}^{3+} \rightarrow 3 \text{ Ni}^{2+} + 1 \text{ Co}^{4+} \rightarrow 1 \text{ Ni}^{3+} + 2 \text{ Mn}^{4+} \rightarrow 2 \text{ Ni}^{3+}$	-5259.751
(2)	$2 \operatorname{Ni}^{3+} \rightarrow 2 \operatorname{Ni}^{2+} + 2 \operatorname{Mn}^{4+} \rightarrow 2 \operatorname{Ni}^{3+}$	-5251.942
(3)	$1 \text{ Ni}^{3+} \rightarrow 1 \text{ Ni}^{2+} + 1 \text{ Co}^{2+} \rightarrow 1 \text{ Ni}^{3+}$	-5243.705

Table S5. Total Coulomb-energy (E_c) for NCM92 in different redox mechanisms (RM).

		Befor	After 300 Cycles			
Sample	Pristine CG- NCM92	MP- 1@CG- NCM92	MP- 2@CG- NCM92	MP- 3@CG- NCM92	Pristine CG- NCM92	MP- 2@CG- NCM92
$R_b(\Omega)$	2.50	2.46	1.69	1.80	4.19	3.90
$R_{CEI}(\Omega)$			_	_	5.55	5.10
R _{int} (Ω)					25.19	20.35
$R_{ct}(\Omega)$	214.80	143.00	124.00	157.90	850	220

Table S6. Fitting results of EIS spectra for pristine CG-NCM92 and MP-x@CG-NCM92electrodes before cycling and after 300 cycles.

Table S7. The total exothermic heat generation (Q_t) and heat reduction of the pristine CG-
NCM92//Li coin-type cell and MP-2@CG-NCM92//Li coin-type during
charge/discharge processes at 35 °C.

		* Q t	Heat r	eduction
Total heat generation Electrode	$(J g^{-1})$		vs. Pristine CG- NCM92	
	Charge	Discharge	Charge	Discharge
Pristine CG-NCM92	-139.00	-119.20		
MP-2@CG-NCM92	-97.88	-83.97	29.6%	29.5%

*A negative Q_t value indicates an exothermic heat release.

	Pristine CG-NCM92			MP-2@CG-NCM92		
	Lithiated Delithiated		Δ_{\max} (%)	Lithiated	Delithiated	Δ_{\max} (%)
	state	state		state	state	
c-axis (Å)	14.443	14.357	0.60	14.505	14.443	0.43
<i>a</i> -axis (Å)	2.848	2.832	0.56	2.843	2.829	0.49
Unit-cell	100.604	99.815	0.78	100.696	100.283	0.41
volume (Å ³)						

Table S8 The in-operando XRD lattice parameters for pristine CG-NCM92 and MP-2@G-
NCM92 electrodes during charging/discharging process.

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