Supporting information

Ultra-high nickel cobalt-free cathode material toward highenergy and long-cycle stable Li-ion batteries: a single-crystal and surface high-entropy design strategy

Jianyao Ma^a, Xin Huang^a, Ruijian Huang^a, Yang Tang^a, Shengyi Huang^a, Yuhang Wang^a, Bin Huang^a, Jianwen Yang^a, Yanwei Li^{a,*}, Meng Qin^{b,*} and Shunhua Xiao^{a,*}

^a Guangxi Colleges and Universities Key Laboratory of Surface and Interface Electrochemistry, Guangxi Key Laboratory of Electrochemical and Magnetochemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, Guangxi, China

^b Liuzhou Gotion Battery Co.,Ltd, Liuzhou 545616, Guangxi, China

*Corresponding Authors: Shunhua Xiao (1999014@glut.edu.cn);Yanwei Li (lywhit@126.com); Meng Qin (qinmeng@gotion.com.cn)

Experimental Section

Synthesis Method: The precursor Ni_{0.9}Mn_{0.1} (OH)₂ and Mg(NO₃)₂, C₁₀H₅NbO₂₀ · xH₂O, C₉H₂₁AlO₃ according to the molar ratio (Ni + Mn) : Mg : Nb : Al = 1 : 0.005 : 0.0025 : 0.01 ratio. The precursor and Mg(NO₃)₂, C₁₀H₅NbO₂₀ · xH₂O in accordance with the ratio of the total amount of about 5g into a beaker, adding anhydrous ethanol 20 mL ultrasonic 30 min, stirring in a water bath at 65 °C heating until evaporated. The dry mixture and LiOH · H₂O molar ratio Ni : Li = 1 : 1.05 were weighed, and then the cosolvent (KCl + LiCl) was weighed.

The mass ratio of the cosolvent to the dry mixture was 0.3 : 1 (the molar ratio of the cosolvent was KCl : LiCl = 1 : 1), which was put into the ball mill together. The mixed powder after ball milling was placed in a tube furnace at 2 °C/min to 500 °C and calcined at this temperature for 300 min, and then heated to 820 °C at 5 °C/min and calcined at this temperature for 900 min, followed by natural cooling. Oxygen (1.5 L/min) was continuously introduced during calcination. Single crystal SC-LNM-MN was prepared. The SC-LNM-MN and C₉H₂₁AlO₃ were put into a glass bottle with anhydrous ethanol, sealed and stirred for 10 h, and then transferred to an oil bath pot for evaporation at 70 °C, and then annealed at 500 °C for 300 min in a tube furnace in an oxygen atmosphere to obtain SHE-SC-LNM.

Material Characterization: The crystal structure of the materials was characterized using an X-ray diffractometer (XRD, X'Pert PRO MRD, PANalytical, Netherlands). Lattice parameters were refined through the Rietveld refinement method utilizing the General Structure Analysis System (GSAS-II) software. The morphology, microstructure, and elemental distribution of the samples were examined via transmission electron microscopy (TEM, FEI Talos F200x) and high-resolution field-emission scanning electron microscopy (FESEM, Hitachi S-4800), both equipped with energy-dispersive spectroscopy (EDS) analyzers. Surface chemical composition was performed using X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific Nexsa).

Electrochemical Testing: The cathode was fabricated by mixing the active material, acetylene black (ECP-600JD), and polyvinylidene fluoride (PVDF 900) in a weight ratio of 8 : 1 : 1 with N-methyl-2-pyrrolidone (NMP) as the solvent to obtain a homogeneous slurry. Next, the slurry was evenly coated onto aluminum foil with a coating weight of approximately 3 mg cm⁻². After being dried under vacuum at 110 °C for an entire night, the coated foil underwent roll pressing and was subsequently punched into disks with a diameter of 12

millimeters. Inside an argon-filled glove box, the CR2032 coin-type half-cells were assembled using a cathode, a lithium metal anode, a Celgard 2400 separator, and an electrolyte composed of a 1 M LiPF₆ solution dissolved in a 1:1:1 molar ratio mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate. For the construction of full-cells, graphite anode material. Galvanostatic charge/discharge (SM0206) served as the tests were conducted across various voltage ranges (2.7-4.3 V, 2.7-4.4 V or 2.7-4.5) and at current densities of 0.1 C, 0.5 C, 1.0 C or 5.0 C (where 1.0 C is equivalent to 210 mA g^{-1}) at a temperature of 25 °C, utilizing a BTS-4000 battery testing system manufactured by Neware (Shenzhen, China). The rate performance was assessed using a current profile that incremented from 0.1 C to 0.2 C, 0.5 C, 1.0 C, 2.0 C, 5.0 C, and 10 C, subsequently returning to 0.1 C. Cyclic voltammetry (CV) was carried out a scan rate of 0.1 mV s⁻¹ utilizing a CHI760E workstation. Electrochemical impedance spectroscopy (EIS) measurements were conducted on the same workstation across a frequency range spanning from 10^{-2} to 10^{5} Hz.

Density Functional Theory (DFT) calculation: We utilized the Vienna Ab initio Simulation Package (VASP)[1,2] to carry out all DFT calculations within the framework of the Generalized Gradient Approximation (GGA), specifically adopting the Perdew–Burke– Ernzerhof (PBE) functional.[3] The Projected Augmented Wave (PAW) approach[4,5] was employed to describe ionic cores, while the valence electrons were handled using a plane-wave basis set with at kinetic energy cutoff of 450 eV. Gaussian smearing, with a width of 0.05 eV, was incorporated to account for the partial occupancies of the Kohn–Sham orbitals. For the purpose of geometry and lattice optimizations, Γ -centered *k*-point sampling was executed at 1 × 1 × 1,[6] achieving self-consistency within an energy tolerance of 10⁻⁵ eV. Once the maximum residual atomic force decreased below 0.02 eV Å⁻¹, the equilibrium configurations were confirmed. A vacuum region of 15 Å was incorporated to mitigate any unwanted interactions among periodic images. The DFT+D3 method, augmented with Grimme's empirical corrections, [7,8] was employed to model weak interatomic forces, and spin polarization was incorporated to account for magnetic phenomena. Furthermore, Vaspkit was leveraged for generating input files and processing charge-difference data. The adsorption energy was calculated using the following formula::

$$Eads = E(*adsorbent) - E(*) - E(adsorbent)$$

Here, E(*adsorbent), E(*), and E(adsorbent) represent the total energies of the adsorbate– surface system, the bare surface, and the isolated adsorbate, respectively. To accurately address the potent on-site Coulomb interactions in transition metals, both structural optimizations and electronic structure calculations were performed using the spin-dependent GGA+U method. Specifically, the effective U_{eff} parameters for Ni and Mn were assigned values of 6.2 eV and 3.9 eV, respectively.[9,10]

Results and Discussion



Figure S1 SEM images of the precursors



Figure S2 Selected area electron diffraction (SAED) pattern of SHE-SC-LNM



Figure S3 SEM images of SC-NM91 (a, b); SEM images of SHE-SC-LNM (c, d)

As shown in Figure S3, the SC-NM91 sample exhibits an uneven particle size distribution and significant local agglomeration, indicating strong interfacial adsorption between particles during high-temperature sintering and a lack of effective morphology control mechanisms. In contrast, the SHE-SC-LNM sample shows a more uniform particle size, good overall dispersion, and minimal observable agglomeration. This improvement is attributed to the surface high-entropy regulation effect: the multi-element composite high-entropy region effectively regulates the nucleation and growth rates of the crystals, suppresses abnormal grain growth, and facilitates the formation of a stable secondary phase coating layer on the crystal surface. This coating reduces the surface energy of the particles and provides spatial separation, thereby effectively inhibiting sintering and agglomeration between particles, ultimately resulting in uniformly distributed, well-defined single-crystal particles.



Figure S4 Magnified EDS image of SHE-SC-LNM



Figure S5 Lattice fringe spacing of SC-NM91 observed under HRTEM



Figure S6 XRD patterns of SHE-SC-LNM and SC-NM91 (a); positions of the (003) peaks for SHE-SC-LNM and SC-NM91 (b); positions of the (104) peaks for SHE-SC-LNM and SC-NM91 (c)



Figure S7 Lattice fringe spacing of γ -Al₂O₃, comparable to the (222) crystal plane spacing of 0.228 nm in

the standard card (JCPDS 29-0063)



Figure S8 XPS spectra of SHE-SC-LNM: Al 2p (a); Mg 1s (b); Nb 3d (c)



Figure S9 Cycling performance of SHE-SC-LNM and SC-NM91: 0.5 C within 2.7-4.3 V (a); 0.5 C within

2.7–4.4 V (b); 0.5 C within 2.7–4.5 V (c)



Figure S10 The d*Qm*/d*V* vs. voltage plot: phase transition shift after 300 cycles for SC-NM91 (a); phase transition shift after 300 cycles for SHE-SC-LNM (b); H2–H3 phase transition positions for SC-NM91 (c); H2–H3 phase transition positions for SHE-SC-LNM (d)



Figure S11.1 Voltage versus time profiles for SHE-SC-LNM and SC-NM91 during a single charge/discharge cycle (a); $Log(D_{Li^+})$ versus time profiles for SHE-SC-LNM and SC-NM91 during a single

charge/discharge cycle (b)



Figure S11.2 Voltage versus time profile for a single pulse of SC-NM91 (a); voltage versus time profile for a single pulse of SHE-SC-LNM (b); voltage versus $\tau^{1/2}$ relationship for SC-NM91 (c); voltage versus $\tau^{1/2}$

relationship for SHE-SC-LNM (d)



Figure S12 EIS spectra of SC-NM91 after the 1st, 100th, 200th, and 300th cycles (a); EIS spectra of SHE-SC-LNM after the 1st, 100th, 200th, and 300th cycles (b)



Figure S13 In situ electrochemical XRD dQ/dV versus voltage profiles for the first charge/discharge cycle of SHE-SC-LNM and SC-NM91 (a)

o



Figure S14 Total density of states (TDOS) for SC-NM91 and SHE-SC-LNM



Figure S15 Density of states (DOS) of the O-2p orbitals for SHE-SC-LNM and SC-NM91

Reagents	Purity	Manufacturer				
Ni0.90Mn0.10(OH)2	/	Guangdong Canrd New Energy Technology Co., Ltd.				
LiOH·H ₂ O	A.R 98%	Xilong Scientific Co.,Ltd.				
Mg(OH) ₂	A.R.	Aladdin Chemistry Co., Ltd.				
$C_{10}H_5NbO_{20}\cdot xH_2O$	A.R 98%	Aladdin Chemistry Co., Ltd.				
$C_9H_{21}AlO_3$	A.R 99.99%	Aladdin Chemistry Co., Ltd.				
NMP	A.R.	Guangdong Canrd New Energy Technology Co., Ltd.				
PVDF	Battery Grade	Guangdong Canrd New Energy Technology Co., Ltd.				
Cochin black	Battery Grade	Guangdong Canrd New Energy Technology Co., Ltd.				

Table S1 The list of main reagents for the experiment

Sample		SHE-HE-LNM					
Crystal system			Rhombohedral				
Space	group		R-3m (166)				
Atom	Wyck	X	У	Z	fraction		
Li1	3b	0.0000	0.0000	0.5000	0.9636		
Ni1	3a	0.0000	0.0000	0.0000	0.8461		
Li2	3a	0.0000	0.0000	0.0000	0.0364		
Ni2	3b	0.0000	0.0000	0.5000	0.0364		
Mn1	3a	0.0000	0.0000	0.0000	0.1000		
Mg1	3a	0.0000	0.0000	0.0000	0.0050		
Nb1	3a	0.0000	0.0000	0.0000	0.0025		
A11	3a	0.0000	0.0000	0.0000	0.0100		
01	6c	1.0000	0.0000	0.257548	1.0000		
<i>a</i> = <i>b</i>			2.8	3784 Å			
С		14.2128 Å					
Li/Ni disorder		3.64%					
R_p		1.7991%					
R_{wp}			2.4431%				
GOF			1.2855%				

 Table S2 Powder X-ray diffraction and refined crystallographic parameters for SHE-SC-LNM

Sample		SC-NM91					
Crystal system		Rhombohedral					
Space	group		R-3m (166)				
Atom	Wyck	x	У	Z	fraction		
Li1	3b	0.0000	0.0000	0.5000	0.9470		
Ni1	3a	0.0000	0.0000	0.0000	0.8470		
Li2	3a	0.0000	0.0000	0.0000	0.0530		
Ni2	3b	0.0000	0.0000	0.5000	0.0530		
Mn1	3a	0.0000	0.0000	0.0000	0.1000		
01	6c	1.0000	0.0000	0.240928	1.0000		
<i>a</i> = <i>b</i>		2.8748 Å					
С		14.2017 Å					
Li/Ni disorder		5.30%					
R_p			2.3140%				
R_{wp}			3.5770%				
GOF			1.8002%				

Table S3 Powder X-ray diffraction and refined crystallographic parameters for SC-NM91

 Sample	$R_{s}\left(\Omega ight)$	$R_{ct}(\Omega)$
 SHE-SC-LNM (1th)	7.40	33.19
SHE-SC-LNM (100th)	2.63	53.36
SHE-SC-LNM (200th)	3.33	74.13
SHE-SC-LNM (300th)	1.91	102.00

 Table S4 Fitted EIS parameters of SHE-SC-LNM after different cycle numbers

Sample	$R_{s}\left(\Omega ight)$	$R_{ct}(\Omega)$
SC-NM91 (1th)	2.68	37.26
SC-NM91 (100th)	4.99	58.40
SC-NM91 (200th)	1.55	102.00
SC-NM91 (300th)	2.40	199.00

Table S5 Fitted EIS parameters of SC-NM91 after different cycle numbers

Sample	1 st capacity (mAh g ⁻¹)	Voltage range (V)	Charge/Discharge current rate (mA g ⁻¹)	Capacity retention/ cycles	Ref.
	176	2.7-4.3		97.7%/100	
SHE-SC-LNM	196	2.7-4.4	1.0 C/1.0 C (210)	94.2%/100	This work
	200	2.7-4.5		92.8%/100	
	176	2.7-4.3		90.1%/300	
SHE-SC-LNM	196	2.7-4.4	1.0 C/1.0 C (210)	88.7%/300	This work
	200	2.7-4.5		85.8%/300	
	196	2.7-4.3		95.5%/100	
SHE-SC-LNM	209	2.7-4.4	0.5 C/0.5 C (210)	93.9%/100	This work
	216	2.7-4.5		90.0%/100	
	196	2.7-4.3		89.8%/200	
SHE-SC-LNM	209	2.7-4.4	0.5 C/0.5 C (210)	89.7%/200	This work
	216	2.7-4.5			
SC-NM91	179	3.0-4.3	1.0 C/1.0 C (200)	85.3%/300	[11]
SCN95-Sr-3	198	2.8-4.3	1.0 C/1.0 C (220)	76.0%/300	[12]
SC-NCM-AS	196	2.75-4.3	1.0 C/1.0 C (200)	91.1%/100	[13]
SC-NCM@CG2	194	2.75-4.3	1.0 C/1.0 C (200)	90.2%/100	[14]
SC-Ni93-ZA	199	2.75-4.4	1.0 C/1.0 C (200)	84.7%/200	[15]
NCMY	196	2.8-4.3	1.0 C/1.0 C (220)	82.7%/150	[16]
CNCM@Nb-2	197	2.7-4.3	1.0 C/1.0 C (200)	92.5%/100	[17]
NM90-1%AB	200	2.7-4.3	1.0 C/1.0 C	86.5%/300	[18]
NCMCs@PMMA	195	2.8-4.3	1.0 C/1.0 C	78.1%/300	[19]

 Table S6 Comparison of cycling stability between SC-NCM-AS and other reported Ni-rich cathode

materials (as cathodes in coin-type half-cells)

NCM9622	199	2.7-4.4	1.0 C/1.0 C	95.7%/100	[20]
NCM-L0.5	174	3.0-4.3	2.0 C/2.0 C	84.5%/200	[21]
SC-NCM90	190	2.7-4.3	0.5 C/0.5 C	75.0%/100	[22]
S-NCM90	190	2.7-4.3	0.5 C/0.5 C	80.7%/100	[23]
Sn-NCM90	214	2.7-4.3	0.5 C/0.5 C	92.9%/100	[24]
NCA95+B1.5%	217	2.7-4.3	0.5 C/0.5 C	87.7%/100	[25]
W-NCA89	218	2.7-4.3	0.5 C/0.5 C	93.6%/100	[26]
4-Al-NCA	207	2.7-4.3	0.5 C/0.5 C	92.6%/100	[27]
NM90	205	2.7-4.3	0.5 C/0.5 C	91.3%/100	[28]
AZO-LRM	217	2.0-4.6	0.5 C/0.5 C	91.1%/200	[29]
Ta-NCA	194	2.8-4.3	0.5 C/0.5 C	93.6%/100	[30]

References

[1] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Computational materials science 6 (1996) 15-50, <u>https://doi.org/10.1016/0927-0256(96)00008-0</u>.

[2] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Physical review B 54 (1996) 11169, https://doi.org/10.1103/PhysRevB.54.11169.

[3] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Physical review letters 77 (1996) 3865, <u>https://doi.org/10.1103/PhysRevLett.77.3865</u>.

[4] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmentedwave method, Physical review b 59 (1999) 1758, <u>https://doi.org/10.1103/PhysRevB.59.1758</u>.

[5] P.E. Blöchl, Projector augmented-wave method, Physical review B 50 (1994) 17953, https://doi.org/10.1103/PhysRevB.50.17953.

[6] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Physical review B 13 (1976) 5188, <u>https://doi.org/10.1103/PhysRevB.13.5188</u>.

[7] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, The Journal of chemical physics 132 (2010), <u>https://doi.org/10.1063/1.3382344</u>.

[8] S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, Journal of computational chemistry 32 (2011) 1456-1465, https://doi.org/10.1002/jcc.21759.

[9] V. Wang, N. Xu, J.-C. Liu, G. Tang, W.-T. Geng, VASPKIT: A user-friendly interface facilitating high-throughput computing and analysis using VASP code, Computer Physics Communications 267 (2021) 108033, <u>https://doi.org/10.1016/j.cpc.2021.108033</u>.

[10] J.M. Munro, K. Latimer, M.K. Horton, S. Dwaraknath, K.A. Persson, An improved symmetry-based approach to reciprocal space path selection in band structure calculations, npj Computational Materials 6 (2020) 112, <u>https://doi.org/10.1038/s41524-020-00383-7</u>.

[11] P. Dai, X. Kong, H. Yang, J. Li, J. Zeng, J. Zhao, Single-crystal Ni-rich layered LiNi_{0.} ₉Mn_{0. 1}O₂ enables superior performance of Co-free cathodes for lithium-ion batteries, ACS Sustainable Chemistry & Engineering 10 (2022) 4381-4390, <u>https://doi.org/10.1021/acssuschemeng.1c06704</u>.

[12] T. Lai, A. Sheng, Z. Zhang, W. Li, J. Yang, S. Zhong, Y. Li, Y. Pei, B. Huang, Effects of strontium oxide on synthesis and performance of monocrystalline ultrahigh-Ni layered cathode materials for Li-ion batteries, Journal of Power Sources 590 (2024) 233811, https://doi.org/10.1016/j.jpowsour.2023.233811. [13] J. Li, W. Zhong, Q. Deng, Q. Zhang, Z. Lin, C. Yang, Mechanistic origin for high structural stability of single crystalline nickel - rich cathode materials via Al and Sm co-doping, Advanced functional materials 33 (2023) 2300127, https://doi.org/10.1002/adfm.202300127.

[14] J. Li, H. Yang, Q. Deng, W. Li, Q. Zhang, Z. Zhang, Y. Chu, C. Yang, Stabilizing Ni - rich Single - crystalline LiNi_{0.83}Co_{0.07}Mn_{0.10}O₂ Cathodes using Ce/Gd Co - doped High - entropy Composite Surfaces, Angewandte Chemie International Edition 63 (2024) e202318042, <u>https://doi.org/10.1002/anie.202318042</u>.

[15] Z.X. Xu, X.H. Chen, W.G. Fan, M.Z. Zhan, X.L. Mu, H.B. Cao, X.H. Wang, H.Y. Xue, Z.H. Gao, Y.Z. Liang, J.J. Liu, X.H. Tan, F. Pan, High-Entropy Rock-Salt Surface Layer Stabilizes the Ultrahigh-Ni Single-Crystal Cathode, Acs Nano 18 (2024) 33706-33717, https://doi.org/10.1021/acsnano.4c13911.

[16] Z. Luo, H. Li, W. Wang, Z. Fang, B. Zhao, G. Hu, Z. Peng, K. Du, Y. Cao, Mitigating irreversible phase transition of Y-doped LiNi_{0.925}Co_{0.03}Mn_{0.045}O₂ by lattice engineering, Ceramics International 50 (2024) 9535-9547, <u>https://doi.org/10.1016/j.ceramint.2023.12.272</u>.

[17] S. Jamil, M. Fasehullah, B. Jabar, P. Liu, M.K. Aslam, Y. Zhang, S. Bao, M. Xu, Significantly fastened redox kinetics in single crystal layered oxide cathode by gradient doping, Nano Energy 94 (2022) 106961, <u>https://doi.org/10.1016/j.nanoen.2022.106961</u>.

[18] L. Zhang, J.F. Huang, H.Y. Tang, S.Y. Huang, Y. Tang, J.Y. Ma, J.W. Yang, B. Huang, Y.W. Li, S.H. Xiao, B/Al Codoped/Coated Ultra-High Nickel Cobalt-Free Material with Excellent High Voltage/Rate Cycle Stability, Acs Sustainable Chemistry & Engineering 12 (2024) 9168-9179, <u>https://doi.org/10.1021/acssuschemeng.4c01847</u>.

[19] H. Tang, D. Liu, J. Huang, L. Zhang, Y. Tang, B. Huang, Y. Li, S. Xiao, Y. Sun, R. Wang, Excellent structural stability and electrochemical properties of LiNi_{0.9}Co_{0.05}Mn_{0.05}O₂ material by surface Ni²⁺ anchoring and Cs⁺ doping, Chinese Chemical Letters (2024) 109987, https://doi.org/10.1016/j.cclet.2024.109987.

[20] J. Huang, L. Zhang, H. Tang, S. Huang, Y. Tang, J. Ma, B. Huang, Y. Li, Y. Sun, S. Xiao, A Mo/PANI co-modified ultra-high nickel NCM9622 cathode composite with excellent cycle stability and high-rate performance for power batteries, Journal of Materials Chemistry A 12 (2024) 21412-21424, <u>https://doi.org/10.1039/D4TA03016H</u>.

[21] X. Qu, Z. Yu, D. Ruan, A. Dou, M. Su, Y. Zhou, Y. Liu, D. Chu, Enhanced electrochemical performance of Ni-rich cathode materials with Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ coating, ACS Sustainable Chemistry & Engineering 8 (2020) 5819-5830, https://doi.org/10.1021/acssuschemeng.9b05539.

[22] G.-M. Han, Y.-S. Kim, H.-H. Ryu, Y.-K. Sun, C.S. Yoon, Structural stability of singlecrystalline Ni-rich layered cathode upon delithiation, ACS Energy Letters 7 (2022) 2919-2926, <u>https://doi.org/10.1021/acsenergylett.2c01521</u>.

[23] H.-H. Ryu, B. Namkoong, J.-H. Kim, I. Belharouak, C.S. Yoon, Y.-K. Sun, Capacity fading mechanisms in Ni-rich single-crystal NCM cathodes, ACS Energy Letters 6 (2021) 2726-2734, <u>https://doi.org/10.1021/acsenergylett.1c01089</u>.

[24] T.T. Nguyen, U.-H. Kim, C.S. Yoon, Y.-K. Sun, Enhanced cycling stability of Sndoped Li [Ni_{0.90}Co_{0.05}Mn_{0.05}]O₂ via optimization of particle shape and orientation, Chem. Eng. J. 405 (2021) 126887, <u>https://doi.org/10.1016/j.cej.2020.126887</u>.

[25] Y.S. Kim, J.H. Kim, Y.-K. Sun, C.S. Yoon, Evolution of a radially aligned microstructure in boron-doped Li [Ni_{0.95}Co_{0.04}Al_{0.01}]O₂ cathode particles, ACS Applied Materials & Interfaces 14 (2022) 17500-17508, <u>https://doi.org/10.1021/acsami.2c02204</u>.

[26] U.-H. Kim, N.-Y. Park, G.-T. Park, H. Kim, C.S. Yoon, Y.-K. Sun, High-energy W-doped Li [Ni_{0.95}Co_{0.04}Al_{0.01}]O₂ cathodes for next-generation electric vehicles, Energy Storage Mater. 33 (2020) 399-407, <u>https://doi.org/10.1016/j.ensm.2020.08.013</u>.

[27] G.-T. Park, N.-Y. Park, T.-C. Noh, B. Namkoong, H.-H. Ryu, J.-Y. Shin, T. Beierling, C.S. Yoon, Y.-K. Sun, High-performance Ni-rich Li[Ni_{0.9-x}Co_{0.1}Al_x]O₂ cathodes via multistage microstructural tailoring from hydroxide precursor to the lithiated oxide, Energy Environ. Sci. 14 (2021) 5084-5095, <u>https://doi.org/10.1039/D1EE01773J</u>.

[28] H.-H. Ryu, G.-C. Kang, R. Ismoyojati, G.-T. Park, F. Maglia, Y.-K. Sun, Intrinsic weaknesses of Co-free Ni–Mn layered cathodes for electric vehicles, Materials Today 56 (2022) 8-15, <u>https://doi.org/10.1016/j.mattod.2022.03.005</u>.

[29] X. Cheng, Y. Wang, J. Lu, W. Dai, H. Lei, J. Zuo, H. Li, Z. Fu, Regulating oxygen redox reactions in lithium-rich materials via an Al₂O₃-doped ZnO layer for enhanced stability and performance, Journal of Materials Chemistry A 12 (2024) 32871-32884, <u>https://doi.org/10.1039/D4TA06843B</u>.

[30] Y. Liu, W. Che, D. Gao, D. Zhang, C. Chang, Ta doping improves the cyclability and rate performance of a nickel-rich NCA cathode via promoted electronic and cationic conductivity, ACS Sustainable Chemistry & Engineering 10 (2022) 16516-16526, https://doi.org/10.1021/acssuschemeng.2c02794.