Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Mo/PANI co-modified ultra-high nickel NCM9622 cathode composite with excellent cycle stability and high-rate performance for power batteries

Jinfu Huang, [a] Liang Zhang, [a] Hongyu Tang, [a] Shengyi Huang, [a] Yang Tang, [a] Jianyao Ma, [a] Bin Huang, [a] Yanwei Li, *,[a] Yiling Sun, *,[b] Shunhua Xiao,*,[a] and Renheng Wang,*,[b, c]

[a]Guangxi Colleges and Universities Key Laboratory of Surface and Interface Electrochemistry, Guangxi Key Laboratory of Electrochemical and Magneto-chemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, Guangxi, China

[b]Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, Guangdong, China

[c]Key Laboratory of Advanced Electrode Materials for Novel Solar Cells for Petroleum and Chemical Industry of China, School of Chemistry and Life Sciences, Suzhou University of Science and Technology, Suzhou City, Jiangsu Province 215009, P. R. China.

*Corresponding Authors.

E-mail: 1999014@glut.edu.cn, lywhit@126.com,

sunyl@szu.edu.cn, wangrh@szu.edu.cn

GITT test methods

Firstly, the newly assembled half-cells are subjected to three charge-discharge cycles at 0.1 C for initial activation, and then the cells are tested for charge-discharge at a current density of 0.1 C, a pulse time of 10 min, a relaxation time of 30 min, and a voltage window of 2.7-4.4 V. The Li^+ diffusion coefficients (D_{Li+}) can be calculated by the following equations:

$$D_{Li^+} = \frac{4}{\pi\tau}\left[\left(\frac{m_B V_M}{M_B S}\right)\left(\frac{\Delta E_s}{\Delta E_\tau}\right)\right]^2 (\tau << L^2/D)$$

Where m_B is the mass (g) of the active substance, V_m and M_B are the molar volume (cm^3 mol^{-1}) and molecular weight (g mol^{-1}) respectively, S is the electrode area (cm^2), τ is the duration (s) of a single current pulse, ΔE_s is the steady-state voltage difference (V) after relaxation for 30 min, and ΔE_τ is the transient voltage difference (V) after the current pulse. The parameters ΔE_s, ΔE_τ and τ in the formula can be obtained from the single pulse GITT curves of Figs. 6(e-g). Based on the data of discharge voltage (V) and corresponding pulse time (τ) in Fig. 6(e-g), the relationship between the discharge voltage (V) and the square root of pulse time ($\tau^{1/2}$) is obtained, as shown in Fig. 6(i)

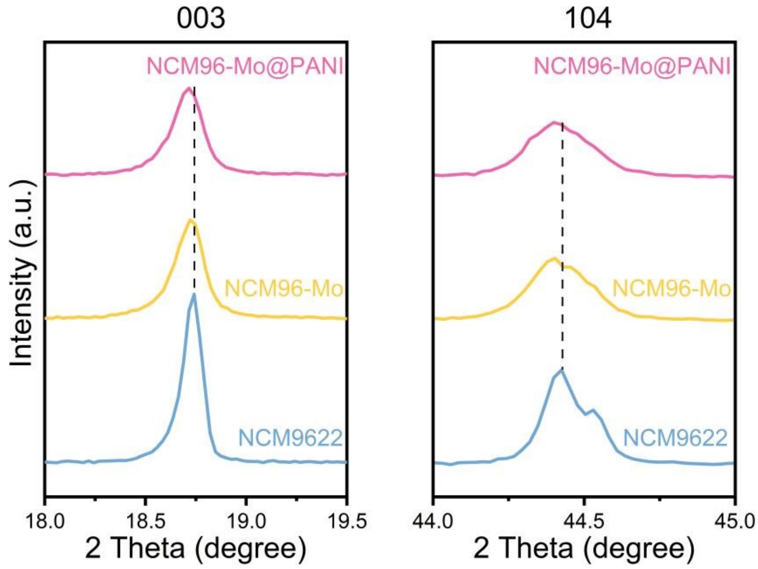

Fig. S1† Enlarged view corresponding to the (003) and (104) diffraction peaks in the XRD pattern.

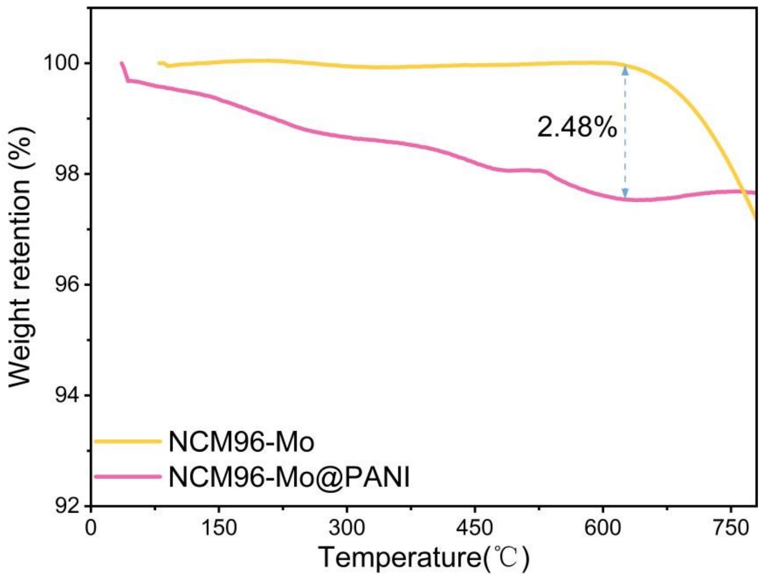

Fig. S2† TGA curves of NCM96-Mo and NCM96-Mo@PANI materials.

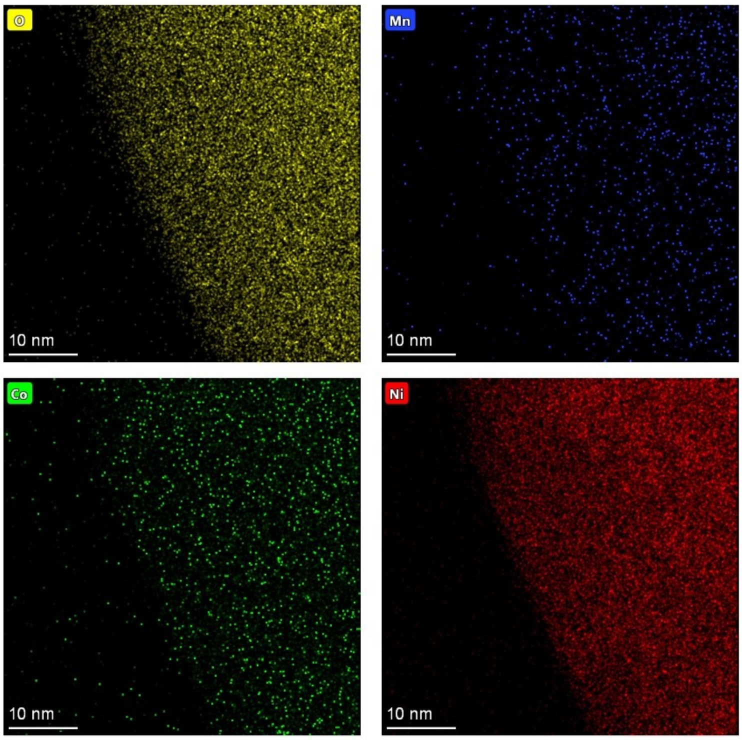

Fig. S3† Mapping of O, Mn, Co and Ni elements of NCM96-Mo@PANI in STEM.

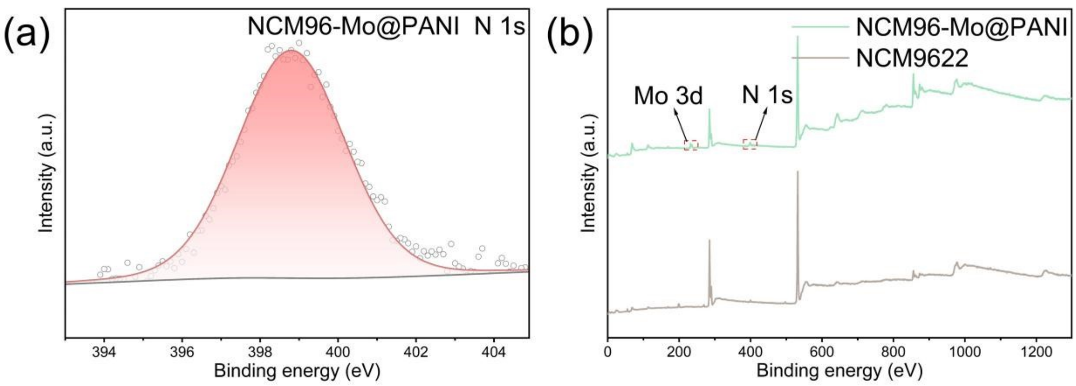

Fig. S4† (a) N 1s XPS spectra of NCM96-Mo@PANI material; (b) XPS full spectra of NCM9622 and NCM96-Mo@PANI materials.

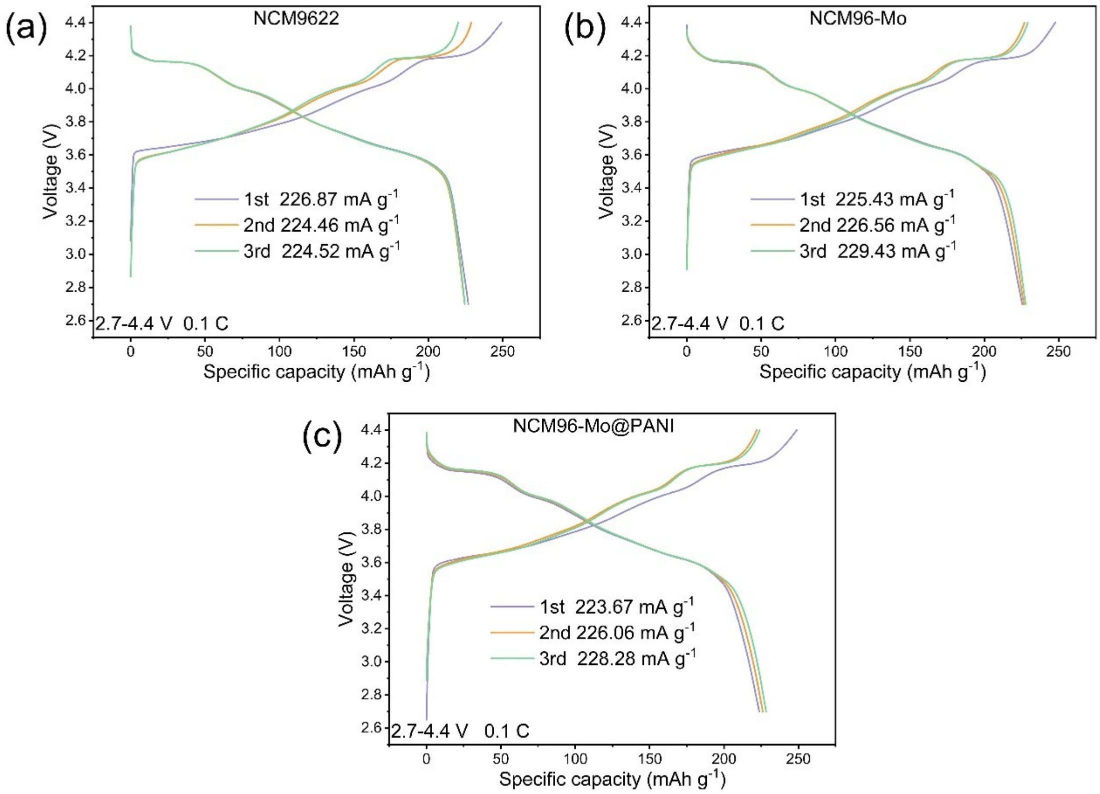

Fig. S5† The first three cycles charge-discharge curves of NCM9622 (a), NCM96-Mo (b) and NCM96-Mo@PANI (c) materials at 2.7-4.4 V and 0.1 C.

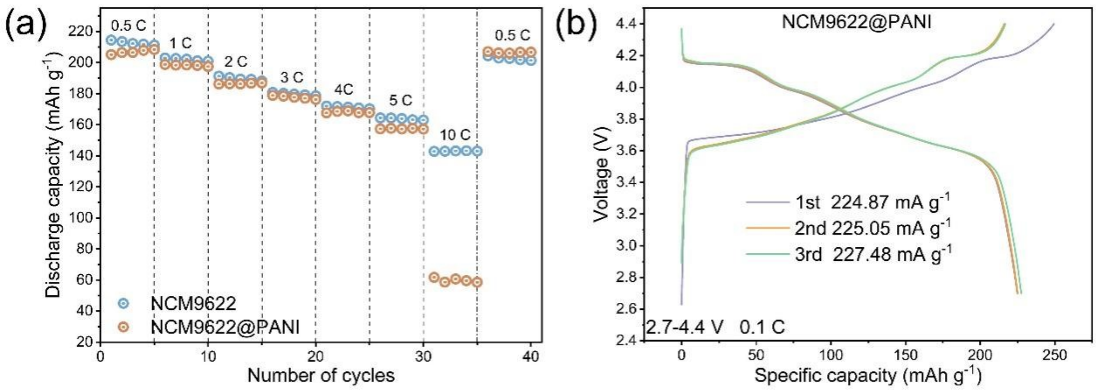

Fig. S6† (a) Rate performances of NCM9622 and NCM9622@PANI materials, and (b) the first three cycles charge-discharge curves of NCM9622@PANI material at 2.7-4.4 V and 0.1 C.

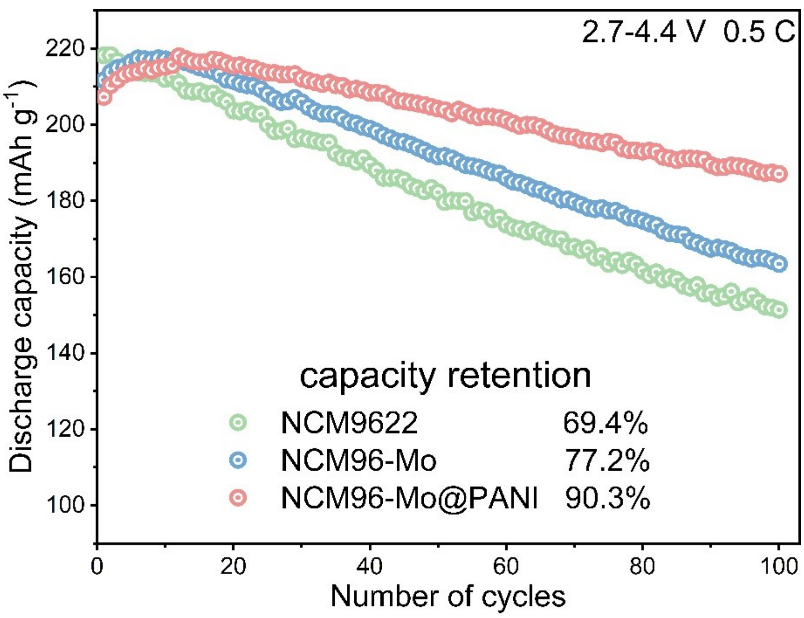

Fig. S7† Cyclic performances of NCM9622, NCM96-Mo and NCM96-Mo@PANI samples at 2.7-4.4 V and 0.5 C.

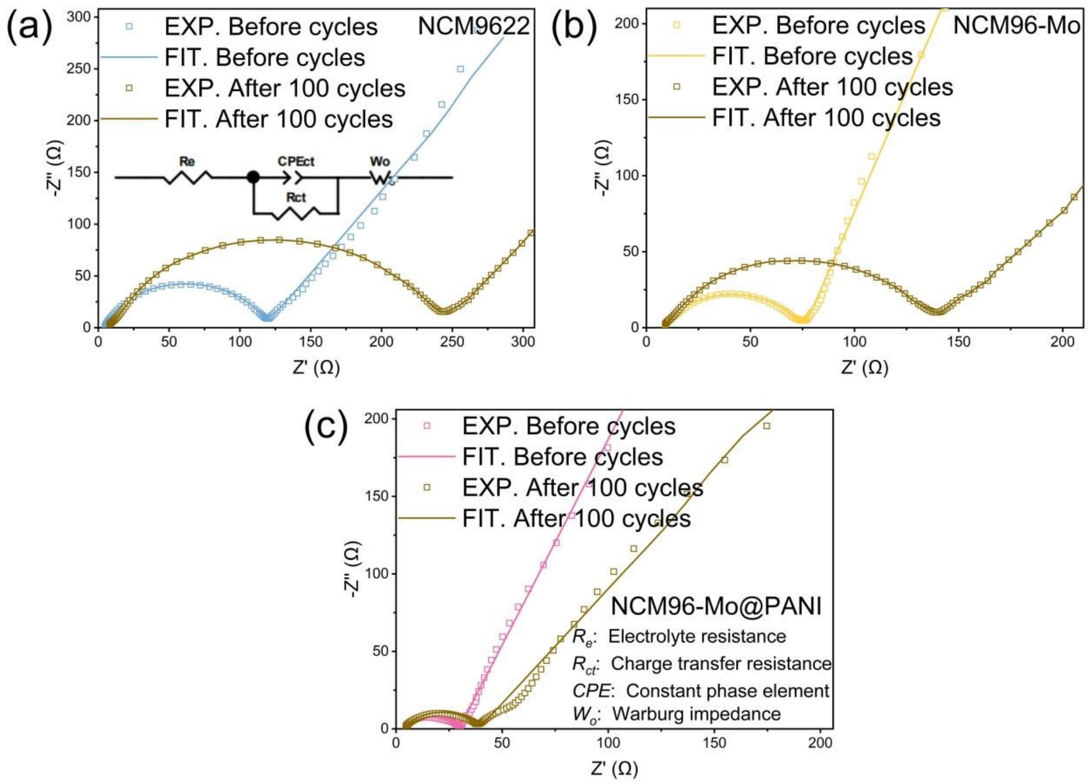

Fig. S8† EIS diagrams of (a) NCM9622, (b) NCM96-Mo and (c) NCM96-Mo@PANI materials before and after 100 cycles at 1 C.

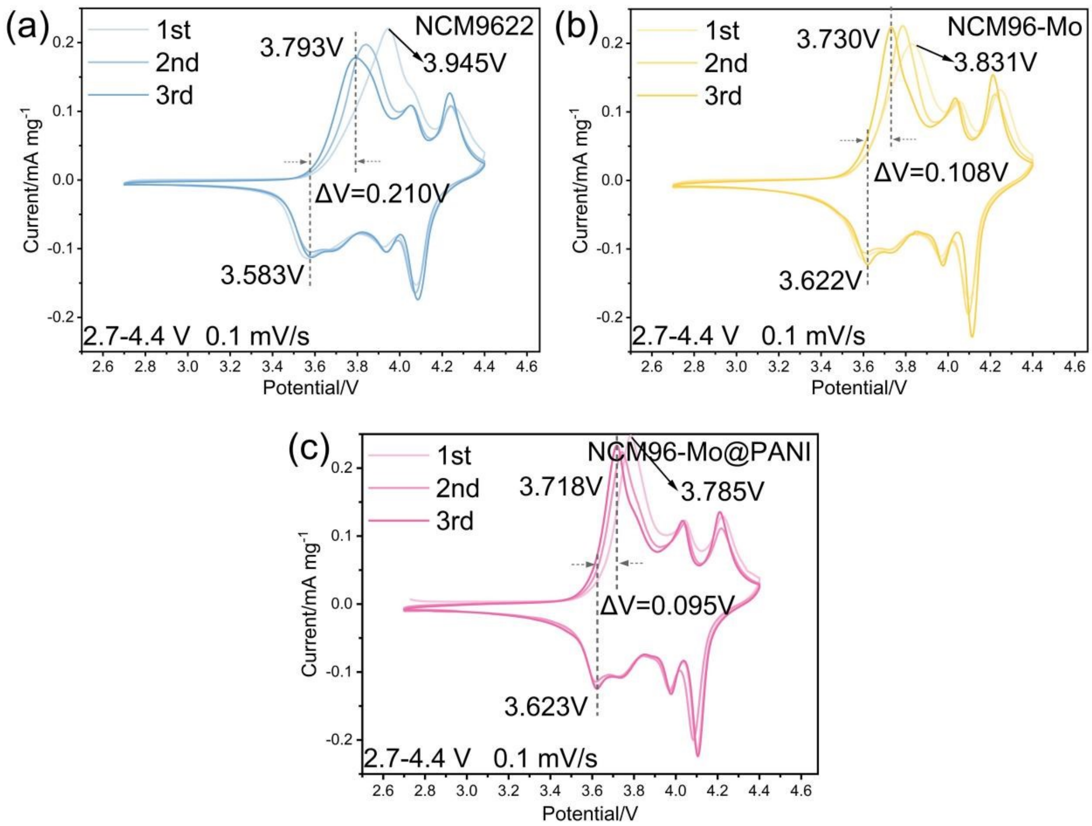

Fig. S9† CV curves of (a) NCM9622, (b) NCM96-Mo, (c) NCM96-Mo@PANI materials at the first three cycles.

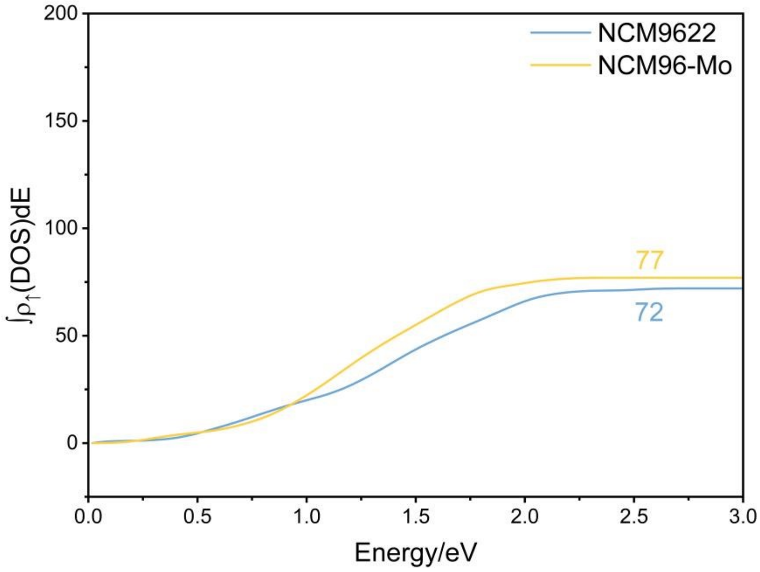

Fig. S10† Integral results of the spin-up total density of states (TDOS) of NCM9622 and NCM96-Mo materials between 0 and 3 eV

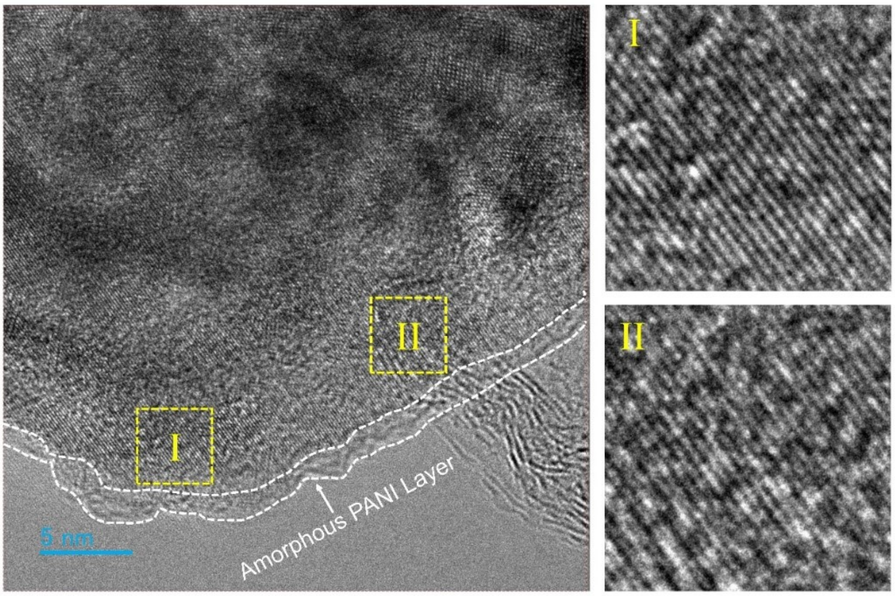

Fig. S11† TEM image of NCM96-Mo@PANI material after 100 cycles at 1 C

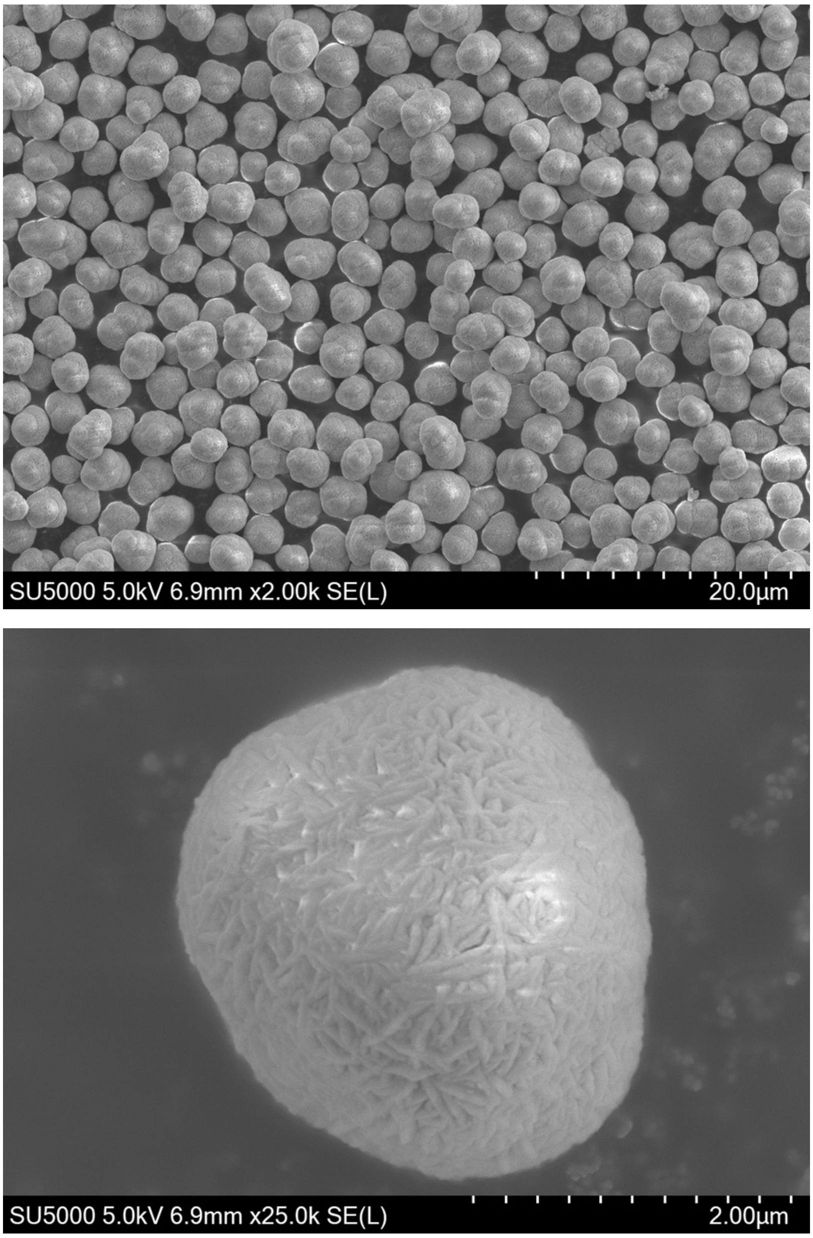

Fig. S12† SEM image of $Ni_{0.96}Co_{0.02}Mn_{0.02}(OH)_2$ precursor

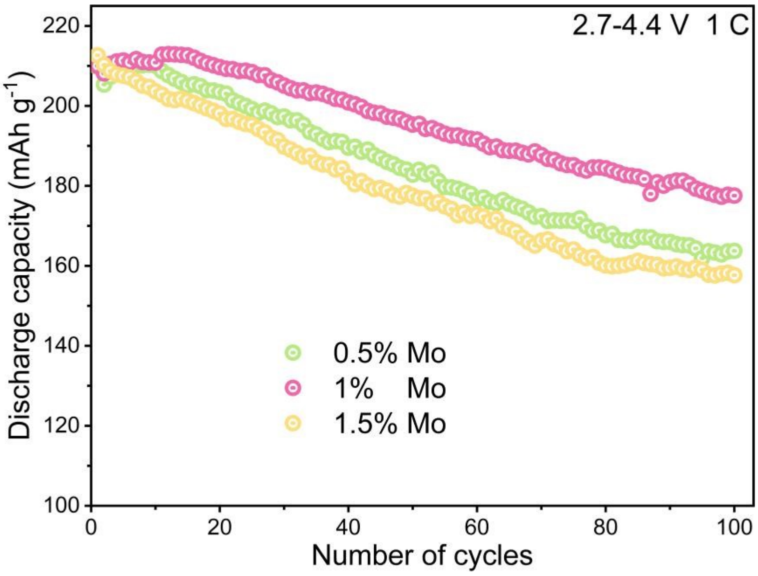

Fig. S13† Cycling performances of NCM96-Mo material with 0.5%, 1% and 1.5%Mo doping.

Table S1† Rietveld refinement data of materials

Samples	*a*=*b* (Å)	*c* (Å)	*c*/*a*	*V* (Å^3)	Li/Ni exchange (%)	R_{wp} (%)
NCM9622	2.87228	14.18206	4.937562	101.327	2.39%	6.3
NCM96-Mo	2.87478	14.19823	4.938893	101.619	3.45%	6.4
NCM96-Mo@PANI	2.87426	14.20372	4.941696	101.621	3%	6.3

Table S2† Comparison of cycling stability of NCM96-Mo@PANI cathode with the Ni-rich cathodes reported before.

Samples	100^{th} capacity retention/rate	The range of operating voltage/V	References
NCM96-Mo@PANI	90.3%/0.5 C	2.7-4.4	This work
Ti-NM90	88.9%/0.5 C	2.7-4.4	1
Al-NM90	88.2%/0.5 C	2.7-4.4	1
Sn-NCM90	87.9%/0.5 C	2.7-4.4	2
Co-NM90	86.3%/0.5 C	2.7-4.4	1
LWO-NCM90	84.6%/0.5 C (80^{th})	3.0-4.3	3
Ga-NCA94	84.4%/0.5 C	2.7-4.3	4
Zr-NCA94	79.2%/0.5 C	2.7-4.3	4

References:

1 Y. J. Sun, C. H. Wang, W. J. Huang, G. F. Zhao, L. Y. Duan, Q. Liu, S. M. Wang, A. Fraser, H. Guo and X. L. Sun, *Angewandte Chemie-International Edition*, 2023, **62**, 202300962

2 G.-T. Park, B. Namkoong, S.-B. Kim, J. Liu, C. S. Yoon and Y.-K. Sun, *Nature Energy*, 2022, **7**, 946-954

3 S. Jamil, A. Bin Yousaf, S. Hee Yoon, D. Suk Han, L. Yang, P. Kasak and X. Wang, *Chemical Engineering Journal*, 2021, **416**, 129118

4 W. M. Seong, K.-H. Cho, J.-W. Park, H. Park, D. Eum, M. H. Lee, I.-s. S. Kim, J. Lim and K. Kang, *Angewandte Chemie International Edition*, 2020, **59**, 18662-18669

5 U.-H. Kim, N.-Y. Park, G.-T. Park, H. Kim, C. S. Yoon and Y.-K. Sun, *Energy Storage Materials*, 2020, **33**, 399-407

6 S.-B. Lee, N.-Y. Park, G.-T. Park, U.-H. Kim, S.-J. Sohn, M.-S. Kang, R. M. Ribas, R. S. Monteiro and Y.-K. Sun, *ACS Energy Letters*, 2024, **9**, 740-747

7 T. Thien Nguyen, U.-H. Kim, C. S. Yoon and Y.-K. Sun, *Chemical Engineering Journal*, 2021, **405**, 126887

8 S.-J. Sim, S.-H. Lee, B.-S. Jin and H.-S. Kim, *Journal of Power Sources*, 2021, **481**, 229037

9 C.-H. Jung, D.-H. Kim, D. Eum, K.-H. Kim, J. Choi, J. Lee, H.-H. Kim, K. Kang and S.-H. Hong, *Advanced Functional Materials*, 2021, **31**, 2010095

Table S3† Impedance fitting data of NCM9622, NCM96-Mo and NCM96-Mo@PANI materials before and after 100 cycles at 1 C

Samples	Before 100 cycles		After 100 cycles	
	R_e (Ω)	R_{ct} (Ω)	R_e (Ω)	R_{ct} (Ω)
NCM9622	4.356	113.2	7.252	228.1
NCM96-Mo	8.305	63.51	8.346	117.1
NCM96-Mo@PANI	2.888	26.78	3.628	35.46