Supplementary Information (SI) for Inorganic Chemistry Frontiers. This journal is © the Partner Organisations 2025

Supporting Information

Janus Binder Favors Interfacial Protection and Mechanical Stabilization for Li-Rich Layered Oxide Cathodes

Wenhua Cheng,^{a, b ‡} Qingcui Liu,^{a, ‡} Huan Zhou,^a Fengjuan Chen,^b Yudai Huang,*^a and

Anqiang Pan*b

^a State Key Laboratory of Chemistry and Utilization of Carbon Based Energy Resources; College of Chemistry, Xinjiang University, Urumqi, 830017, P. R. China

^b Engineering Research Center of Environmental and Functional Materials, School of Materials

Science and Engineering, Xinjiang University, Urumqi, 830017, Xinjiang, P. R. China

* Corresponding author. E-mail address: huangyd@xju.edu.cn (Prof. Yudai Huang); pananqiang@xju.edu.cn (Prof. Anqiang Pan)

[‡] These authors contributed equally to this work.

Experimental Section

1. Material Synthesis

The carbonate precursor is synthesized via a co-precipitation method. Initially, $MnSO_4 \cdot H_2O$ ($\geq 99\%$, Aladdin) and $NiSO_4 \cdot 6H_2O$ ($\geq 98\%$, Aladdin) were dissolved in deionized water in 3 : 1 molar ratio to form the transition metal mixture solution A (0.1M). Simultaneously, NaHCO₃, with a 10 times the number of moles of the transition metal salts, was dissolved in deionized water to obtain solution B (1M). Next, solution A is rapidly added to solution B while stirring for 4 h. After overnight precipitation, the supernatant was decanted, and the precipitate was filtered and washed three times with deionized water. The resulting solid was then dried at 80 °C for 12 h in the air, followed by vacuum drying at 100 °C for 12 h to obtain the carbonate precursor Mn_{0.75}Ni_{0.25}CO₃.

The Li-rich layered oxide cathode material, $Li_{1.2}Mn_{0.64}Ni_{0.16}O_2$, is synthesized by hightemperature calcination. The carbonate precursor $Mn_{0.75}Ni_{0.25}CO_3$ was mixed with Li_2CO_3 (\geq 99%, Aladdin) (Li excess 5%) in a molar ratio of 1 : 0.75. This mixture was pretreated at 500 °C for 5 h, then calcined at 850 °C for 10 h in the air, followed by natural cooling to room temperature to obtain the $Li_{1.2}Mn_{0.64}Ni_{0.16}O_2$ (LLO).

2. Electrochemical measurements

Preparation of cathode electrodes: The active material, conductive agent (Super P, Timcal), and binder (Carrageenan (\geq 90%, Aladdin) or PVDF (HSV900, Arkema)) were mixed in a mass ratio of 90 : 5 : 5, with deionized water as the solvent for the carrageenan, and NMP as the solvent for the PVDF. The mixtures were milled and blended into a slurry, which was uniformly applied to Al foil collectors. The electrode with PVDF binder was vacuum dried at 110 °C for 12 h, and the electrode with carrageenan binder was dried at 80 °C for 12 h. After drying, the electrodes were cut into discs with a diameter of 1.2 cm. The electrode with carrageenan binder was labeled as LLO-C, and the one with PVDF binder as LLO-P. CR2032-type button cells were assembled in an argon-filled glove box, maintaining a moisture and oxygen content below 0.01 ppm. The electrolyte used was a high-voltage LIBs electrolyte (LB-372, DodoChem). Charge/discharge tests were conducted on a battery test system (LAND, CT2001A) with a voltage range of 2.0-4.8 V. CV tests were carried out within the same voltage range, and EIS tests were performed across a frequency range of 100 kHz to 0.01 Hz with a

voltage amplitude of 5 mV using an electrochemical workstation (CHI760E).

The Li⁺ diffusion coefficient (D_{Li+}) can be calculated from the following two equations.¹ Based on the EIS results, we can plot the real part of the total impedance (Z') against the inverse of the square root of the angular velocity ($\omega^{-0.5}$) to derive the Warburg factor (σ) according to Eq. 1.

$$Z' = R_s + R_{ct} + \sigma \omega^{-1/2}$$
 (Eq. 1)

$$D_{Li^{+}} = \frac{R^2 T^2}{2A^2 n^4 F^4 \sigma^2 C^2}$$
(Eq. 2)

In Eq. 2, the R, T, A, F, C and n represent the gas constant (8.314 J K⁻¹ mol⁻¹), absolute temperature, electrode surface area (1.1304 cm²), Faraday constant (96485 C mol⁻¹), molar concentration of lithium ions (0.0339 mol cm⁻³) and the number of electrons transferred during redox, respectively

3. Characterization

The structures and morphologies were analyzed using a field-emission scanning electron microscope (SEM, Hitachi, S-4800) and a transmission electron microscope (TEM, FEI Tecnai G2 F20). The surface chemistry of the materials was characterized by X-ray photoelectron spectroscopy (XPS, ThermoFisher, Thermo Scientific K-Alpha+) with an Al K α (h ν = 1486.6 eV) microfocus monochromatic source and Fourier transform infrared spectrometer (FTIR, Bruke, VERTEX 70 RAMI). The elemental composition of the samples was determined using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900).

Supporting Figures and Tables



Figure S1. Elemental mapping of active materials in the electrode before cycle: (a) LLO-P

and (b) LLO-C.



Figure S2. The C 1s XPS spectrum of LLOs pristine powder.



Figure S3. Charge/discharge curves during 1 C: (a) LLO-P and (b) LLO-C. The voltage hysteresis curves after 550 cycles at 2 C for (c) LLO-P and (d) LLO-C.



Figure S4. The CV curves of different scanning rates (0.2-1.2 mV s⁻¹) for (a) LLO-P and (b) LLO-C; (c) Assessment of Li⁺ diffusion rates based on CV tests for $Ni^{2+}/Ni^{3+}/Ni^{4+}$ oxidation reactions.



Figure S5. EIS curves and $R_{s},\,R_{ct}$ and $D_{\mathrm{Li^{+}}}$ before cycling for LLO-P and LLO-C.



Figure S6. The TEM images of (a) LLO-P and (b) LLO-C after 100 cycles.

		Elemental content (at%)						
		0	С	Mn	Ni	F	Р	S
LLO-P	Before cycle	55.96	22.24	14.57	4.76	2.48	-	-
	3 cycles	45.10	27.00	11.93	3.95	10.77	1.24	-
	100 cycles	38.55	26.48	10.06	3.29	20.27	1.35	-
LLO-C	Before cycle	64.43	12.68	17.28	5.56	-	-	0.05
	3 cycles	56.03	17.27	15.75	5.04	4.93	0.93	0.06
	100 cycles	57.74	15.58	15.97	5.67	3.95	0.88	0.21

Table S1. Relative elemental content on the surface of the active material before thecycle, after initial 3 cycles, and 100 cycles.

References

 Y. Feng, Y. Ji, C. Gao, B. Chen, Y. He, J. Guo, Z. Guo and H. Huang, Local electronic structure modulation via S substitution enables fast-discharging capability for Li-rich Mn-based oxides cathodes, *J. Energy Storage*, 2024, 102, 113822.