

Supporting information

Superior electrochemical performance of Li-rich layered cathode material with Li-rich spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and MgF_2 double surface modifications

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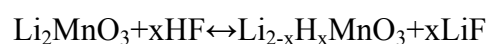
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Experimental section

1. Preparation of materials (LMR, LMR@Spinel, and LMR@Spinel@MgF₂)

The Li-rich layered cathode material Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ was synthesized in a typical combustion method. Stoichiometric amounts of lithium acetate dehydrate with 5 wt% excess, nickel acetate tetrahydrate and manganese acetate tetrahydrate were dissolved in ethanol to form metal ion solution. In the meantime, corresponding stoichiometric amounts of citric acid monohydrate as starting reagent was dissolved in the equal volume of ethanol. Then, two kinds of the solution started complexation reaction through dropwise added respectively in 100ml ethanol at 80°C. After finishing the complexation reaction, the precipitate was evaporated to dryness at 100°C. The dryness was calcined at 450°C for 5h and then at 900°C for 12h to get Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ (LMR) powder. To prepare the LMR@Spinel@MgF₂ material, the LMR@Spinel material was first synthesized in a simple way of liquid-phase erosion. The 0.5g LMR powder was mixed with a certain amount of NH₄F in a certain volume of deionized water under rigorous stirring at 80°C and then sintered at 400°C for 5 h to get the LMR@Spinel material. During this process, the Li-ion in the surface structure of the Li₂MnO₃ component was extracted through Li-H ion exchange and the surface structure of Li_{2-x}H_xMnO₃ transformed from the layered structure to the Li-rich spinel Li₄Mn₅O₁₂ during subsequent heat treatment. Similar reaction mechanisms have been demonstrated in previous literature.^{1,2} Some reactions were as follows:



Thereafter, MgF_2 was coated on the surface of the LMR@Spinel material with a convenient liquid phase deposition method. A certain amount of the LMR@Spinel powder was dispersed in the $\text{Mg}(\text{NO}_3)_2$ dilute aqueous solution and then NH_4F dilute aqueous solution was added drop by drop in the above suspension. After that, the mixture was dried under rigorous stirring at 80°C and sintered at 400°C for 5 h to obtain the LMR@Spinel@ MgF_2 material. The material was synthesized with 1wt% MgF_2 .

2. Material characterization

The crystal structure of the material was performed by X-ray diffraction (XRD, Bruker D8 ADVANCE) with $\text{Cu K}\alpha$ radiation in a range of 10 - 80° . Field-emission scanning electron microscopy (FESEM, JSM-6390) was used to observe the material morphology. The X-ray photoelectron spectroscopy (XPS) was measured by Thermo Fisher ESCALAB Xi+. The microstructure and elemental distribution mapping of the material were studied by field-emission transmission electron microscopy (FE-TEM, JEOL JEM-F200 (HR)) equipped with energy-dispersive X-ray spectroscopy (EDS). Raman scattering was analyzed by Laser Raman Spectrometer with a 532 nm excitation wavelength.

3. Electrochemical measurements

The cathode electrode was prepared including 80wt % active material, 10wt % acetylene black as a conductive additive and 10wt % polyvinylidene fluoride (PVDF) as the binder. The electrochemical performances of all materials were performed with coin-type half cells (2025) at different current rates ($0.1\text{C}=20\text{mA g}^{-1}$) in the voltage window of 2-4.8V at 25°C , which were assembled by inserted the cathode electrode,

polypropylene film as separator and Li metal as an anode electrode. The electrolyte was made by 1 M LiPF₆ dissolved in mixed solvents including diethyl carbonate /dimethyl carbonate/ethylene carbonate with a volume ratio of 1: 1: 1. Galvanostatic intermittent titration technique (GITT) was carried out by the battery test system (Neware, China) to measure Li-ion diffusion behavior of all materials during the first discharge process. After the first charge process, the cell was discharged with an unchanging current flux of 20 mA g⁻¹ for 10 min, followed by an open circuit for 10 min to reach the ready state. Electrochemical impedance spectroscopy (EIS) was analyzed on an electrochemical workstation (CHI660C) by applying an alternating voltage of 5 mV.

To analyze the microstructures of all materials after long cycles, the cycled cells were disassembled in the Ar atmosphere, the powder was peeled off from the electrode and washed four times with dimethyl carbonate. Finally, the cathode powder was dried in the glovebox and then characterized.

Table S1 The lattice parameters and the ratios of c/a for all materials calculated from the XRD data.

Sample	a/Å	c/Å	c/a
LMR	2.8605	14.2549	4.9833
LMR@Spinel	2.8600	14.2683	4.9889
LMR@Spinel@MgF ₂	2.8587	14.2705	4.9919

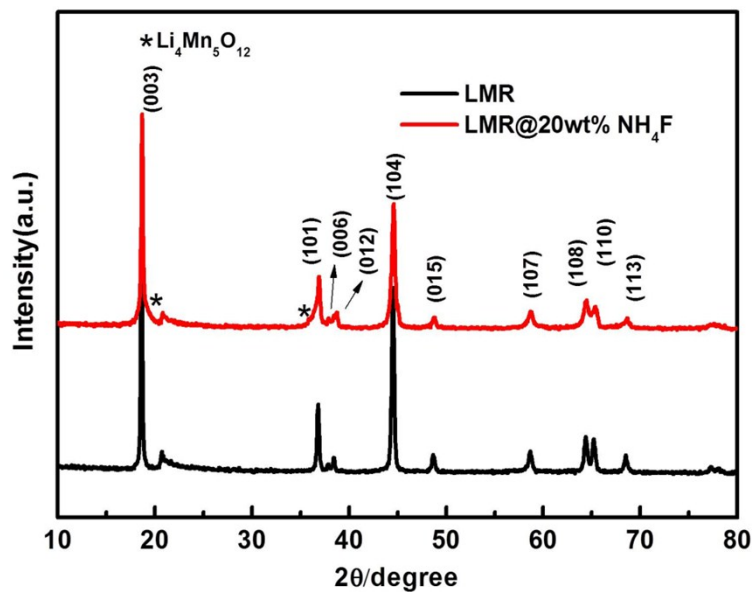


Fig. S1 XRD patterns of LMR and LMR@20wt% NH_4F materials.

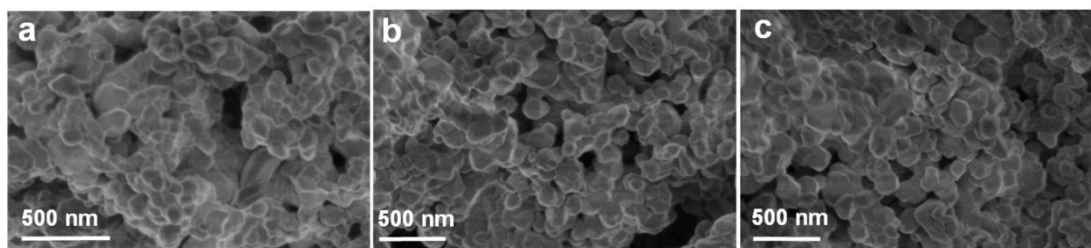


Fig. S2 SEM images of (a) the LMR, (b) LMR@Spinel and (c) LMR@Spinel@ MgF_2 materials.

Table S2 The first discharge capacity in different areas of LMR, LMR@Spinel and LMR@Spinel@ MgF_2 materials

Materials	Capacity above 3.5 V (mAh g^{-1})	Capacity below 3.5 V (mAh g^{-1})
LMR	130.6	122.7
LMR@Spinel	117.1	151.8
LMR@Spinel@ MgF_2	117.5	149.9

Table S3 Voltage decay of Li-rich layered cathode materials

Cathode	Strategy	Voltage decay rate (mV / cycle)	Ref
$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$	$\text{Li}_4\text{Mn}_5\text{O}_{12}/\text{MgF}_2$ surface modification	1.5 (100 mA g^{-1})	This work
$\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.10}\text{Mn}_{0.55}\text{O}_2$	AlF_3 coating	4 (84 mA g^{-1})	3
$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$	Spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ coating	3 (250 mA g^{-1})	4
$\text{Li}_{1.232}\text{Ni}_{0.154}\text{Mn}_{0.615}\text{O}_2$	K^+ doping	6.84 (100 mA g^{-1})	5
$\text{Li}_{1.26}\text{Ni}_{0.07}\text{Co}_{0.07}\text{Mn}_{0.6}\text{O}_2$	Ti^{4+} doping	3.29 (24.8 mA g^{-1})	6
$\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$	CoF_2 coating	3.21 (20 mA g^{-1})	7
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$	Spinel LiMn_2O_4 / carbon coating	3.3 (125 mA g^{-1})	8
$0.4\text{Li}_2\text{MnO}_3\text{-}0.6\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$	Acid treatment and LiCoPO_4 coating	4 (200 mA g^{-1})	9
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$	KF coating	3.1 (125 mA g^{-1})	10
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$	LiCeO_2 coating	2.05 (250 mA g^{-1})	11
$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$	Carbonate co-precipitation	2.75 (40 mA g^{-1})	12

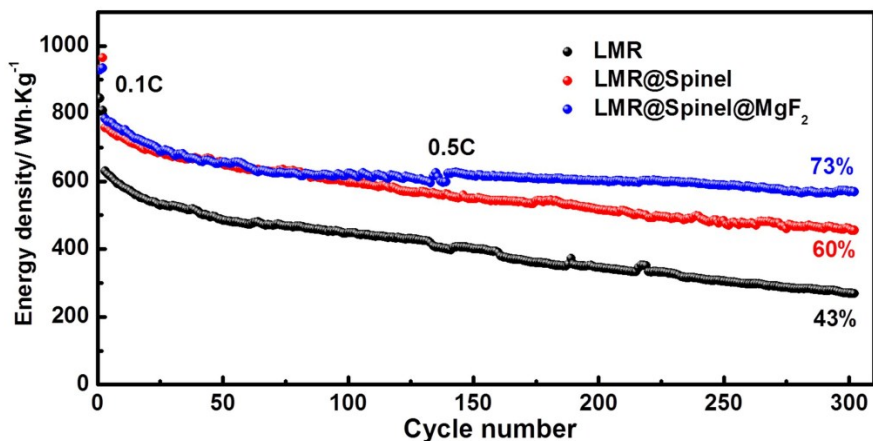


Fig. S3 Cycling performance of energy density for all the materials at 0.5C between 2.0 V and 4.8 V upon cycling after activation at 0.1C for 2 cycles.

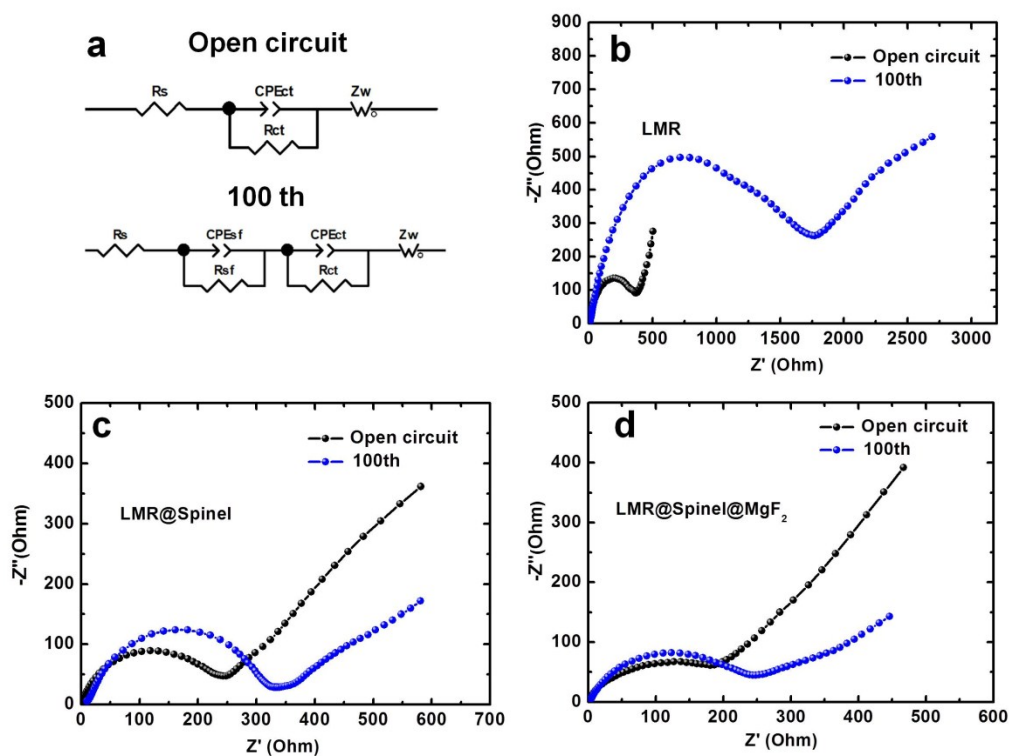


Fig. S4 (a) The equivalent circuit of EIS profiles. (b) EIS profiles of LMR, (c) LMR@Spinel and (d) LMR@Spinel@MgF₂ materials at open circuit potential and after 100 cycles, respectively.

Table S4 The obtained fitting results of EIS spectrums.

Materials	Cycles	Rs(Ω)	Rsf(Ω)	Rct(Ω)
LMR	Open Circuit	1.816	–	350
	100	5.336	1171	1344
LMR@Spinel	Open Circuit	0.81	–	196.3
	100	4.376	98.17	255.9
LMR@Spinel@MgF ₂	Open Circuit	1.496	–	132
	100	6.544	–	207.7

Table S5 The comparison of specific area electron transfer impedance.

Cathode	Strategy	Impedance increase rate ΔR_{ct} ($\Omega \text{ cm}^{-2}$ / cycle)	Ref
Li _{1.2} Ni _{0.2} Mn _{0.6} O ₂	Li ₄ Mn ₅ O ₁₂ /MgF ₂ surface modification	0.67	This work
Li _{1.232} Ni _{0.154} Mn _{0.615} O ₂	K ⁺ doping	2.54	5
Li _{1.2} Ni _{0.2} Mn _{0.6} O ₂	Spinel /Fe ₂ O ₃ surface modification	7.82	13
Li _{1.2} Ni _{0.17} Co _{0.07} Mn _{0.56} O ₂	Li ₂ SiO ₃ coating	78.08	14
Li _{1.2} Ni _{0.13} Co _{0.13} Mn _{0.54} O ₂	LiCeO ₂ coating	2.89	11

Impedance increase rate is the increment of specific area electron transfer impedance per cycle.

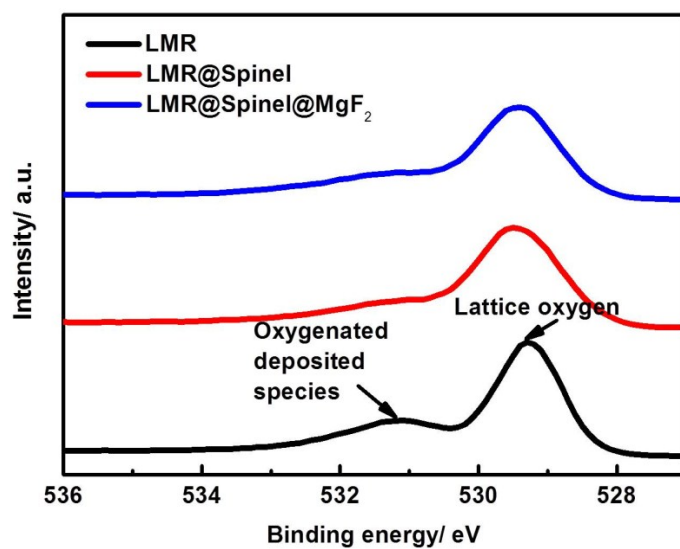


Fig. S5 XPS spectra in the regions of O 1s of the LMR, LMR@Spinel and LMR@Spinel@MgF₂ materials.

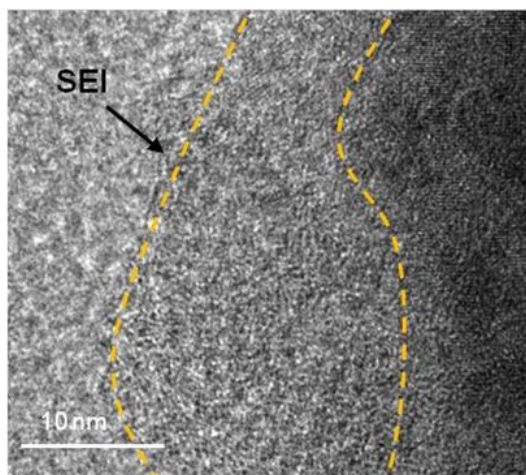


Fig. S6 HRTEM image of the LMR material at full discharge state after 100 cycles.

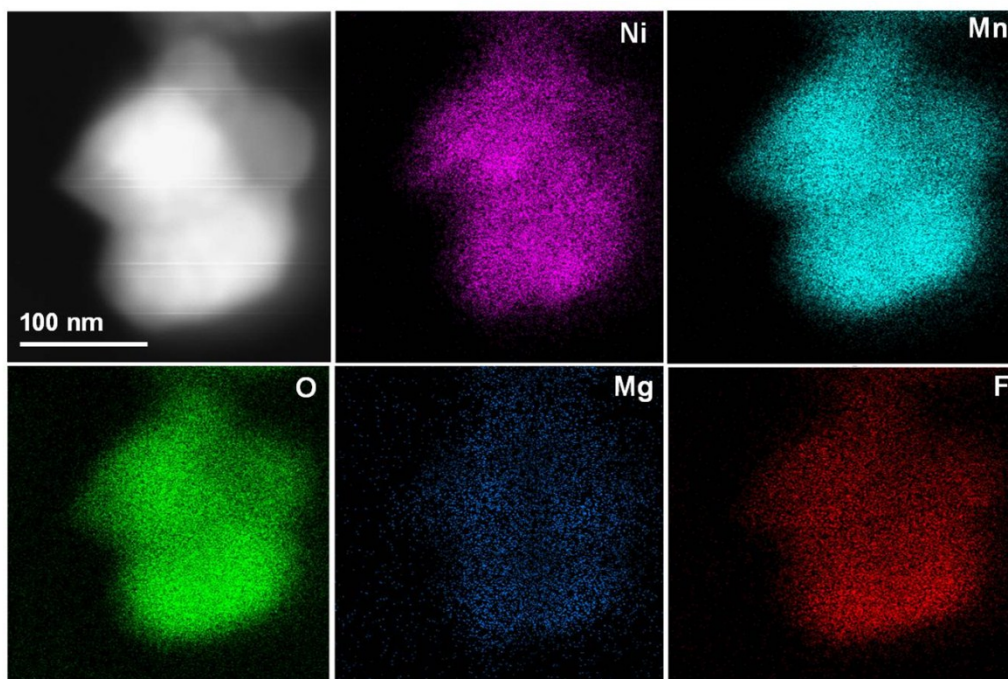


Fig. S7 TEM image and corresponding EDS elemental mapping of the LMR@Spinel@MgF₂ material at full discharge state after 100 cycles.

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