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Supporting Information

For

In-situ Generated Bilayer Functional Coatings on Manganese-Rich

LiMn_{0.84}Fe_{0.15}Mg_{0.01}PO₄ for High-Rate Lithium-Ion Batteries

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Experiments and characterizations

1 Preparation of the L_{1.03}MFMP_{1.01} samples

The LiMn_{0.84}Fe_{0.15}Mg_{0.01}PO₄/C samples were prepared via a simple ball-milling solid-state route assisted with Mg-doping, composite carbon coating, and Li₃PO₄ coating. A vertical high-energy ball mill can achieve nano-level grinding, and the output particle size is less than 1um. A 150mL polytetrafluoroethylene ball milling jar is used, and the matching grinding media is agate balls. Among them, the mass ratio of 6 mm and 12 mm balls is 3:1, and the mass ratio of balls to materials and water is 1:1. Raw materials are LiOH·H₂O (Li source), MnCO₃ (Mn source), FeC₂O₄·2H₂O (Fe source), NH₄H₂PO₄ (P source), MgCl₂·6H₂O, citric acid, and polyethylene glycol 400 (PEG 400), among which MgCl₂·6H₂O is the dopant, and citric acid and PEG 400 are the carbon sources. All reagents used are analytical grade and not purified. The molar ratios for LiOH·H₂O, MnCO₃, FeC₂O₄·2H₂O, MgCl₂·6H₂O, and NH₄H₂PO₄

were 1.03:0.84:0.15:0.01:1.01. Citric acid and PEG 400 account for 2 wt% and 4 wt% of all raw materials, respectively. First, citric acid and PEG400 were added to 40mL of anhydrous ethanol and ball milled at 400rpm for 10min. Then MnCO₃, $FeC_2O_4 \cdot 2H_2O$, MgCl₂·6H₂O, NH₄H₂PO₄, and LiOH·H₂O were added in sequence, and ball milled at 400rpm for 10h. The purpose of adding citric acid and PEG400 first was to create a reducing environment to prevent oxidation of transition metal salts. The homogeneous mixture was immediately dried in an oven at 80 °C, sintered to 650 °C in a N₂ atmosphere tube furnace at a heating rate of 3 °C/min and kept warm for 8 hours. Finally, the positive electrode material was obtained through cooling, grinding and screening, which was denoted as L_{1.03}MFMP_{1.01}.

For comparison, LMFMP, $L_{1.03}$ MFMP, and LMFMP_{1.01} was synthesized using the same process, but the molar ratios of LiOH·H₂O, MnCO₃, FeC₂O₄·2H₂O, MgCl₂·6H₂O, and NH₄H₂PO₄ were 1:0.84:0.15:0.01:1, 1.03:0.84:0.15:0.01:1, and 1:0.84:0.15:0.01:1.01, respectively.

2 Material Characterization.

The structure of the as-prepared samples was analyzed by powder X-ray diffraction (XRD, Bruker D8 Advance) with Cu-Ka radiation of 1.5418 Å incident light, and the samples were refined using the GSAS technique. Fourier transform infrared (FTIR, Thermo Fisher IS10) tests were conducted to investigate the structure. The carbon content was determined using the analytical apparatus of TGA/DSC (METTLER TOLEDO). Raman spectroscopy (Renishaw/invia Qontor) with a 532 nm wavelength laser was employed to characterize the carbon structure. The mobility, carrier concentration and electronic conductivity of the powder samples were evaluated using a Hall effect test system (CH-50) after a 10 MPa pressure compression. The surface area was determined by Brunauer-Emmett-Teller (BET, JW-BK112). Field emission scanning electron microscopy (FESEM, GEMINI500) was used for morphological characterizations. Transmission electron microscopy (TEM, Talos F200X) was used for microstructure analysis. The elemental distribution of the samples was determined by electron diffraction spectroscopy (EDS) mapping analysis. X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB Xi+)

was used to identify the valence state and the related bonds of elements. X-ray fluorescence (XRF, S8 TIGER) spectrometry was used to detect the element content of substances.

3 Electrochemical Measurement.

The acquired samples were used as positive active materials. The working electrode was made by dissolving an electrode with 75 wt % active materials (LMFP, $L_{1.03}$ MFMP, LMFMP_{1.01} or $L_{1.03}$ MFMP_{1.01}), 15 wt % acetylene black, and 10 wt % polyvinylidene fluoride (PVDF) in *n*-methylpyridine (NMP), and coating the slurry on Al foil. The separator was Celgard 2325 membrane. The counter electrode was Li foil. The liquid electrolyte was created by dissolving 1 mol L⁻¹ LiPF₆ in a 1:1 volume mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The above materials were assembled into a CR2016 button cell and sealed at a pressure of 600 psi in an Ar glove box. The cells were charged and discharged between 2.5 and 4.5 V using a battery system (LAND CT2001A, China, $1C = 170 \text{ mA h g}^{-1}$). The cells were charged in constant-current constant-voltage (CCCV) mode and discharged in constant-current (CC) mode, which means that they were charged to 4.5 V at a constant current, then charged to 1/10 of the constant current at 4.5 V, and discharged to 2.5 V at various current densities. Galvanostatic intermittent titration technique (GITT) test of cells was to charge/discharge for 20 min, relax for 120 min at 0.05C and repeat this step to complete a charge-discharge process. An electrochemical workstation (VMP2, Princeton Applied Research) was used for electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tests. EIS was carried out in a frequency range of 10 mHz-100 kHz. CV curves were acquired at a scan rate of 0.10 mV s⁻¹, and in situ EIS was obtained at different potentials simultaneously with the CV tests.

Supply Figures



Figure S1 Rietveld refinement patterns for LMFMP, L_{1.03}MFMP, and LMFMP_{1.01}.



Figure S2 TGA curves for LMFMP and $L_{1.03}MFMP_{1.01}$



Figure S3 BF-STEM micrographs, HAADF-STEM micrographs and TEM-EDS mapping for (a) LMFMP and (b) $L_{1.03}MFMP_{1.01}$.



Figure S4 XPS of O 1s for $L_{1.03}MFMP_{1.01}$



Figure S5 Cyclic voltammetry curve corresponding to in-situ PEIS measurement for (a) LMFMP and (b) $L_{1.03}MFMP_{1.01}$.



Figure S6 The impedances for LMFMP and $L_{1.03}MFMP_{1.01}$ at different potentials.



Figure S7 E vs t profile of $L_{1.03}$ MFMP_{1.01} for a single GITT titration during (a) charge and (c) discharge process. The corresponding linear behavior of the E vs $\tau^{1/2}$ relationship (b, d).



Figure S8 SEM images (a, b) and TEM images (c) for LMFMP after cycling.



Figure S9 XPS spectra of C 1s (a) and P 2p (b) for $L_{1.03}MFMP_{1.01}$ after 500 cycles.



Figure S10 The Z' vs $\omega^{-1/2}$ relationship for (a) LMFMP and (b) $L_{1.03}MFMP_{1.01}.$

table 51 Crystal structure parameters of the four samples							
Samples	a / Å	b / Å	c / Å	Vol. / Å ³	χ^2	R _{wp} / %	
LMFMP	6.085	10.425	4.736	300.48	0.94	3.95	
L _{1.03} MFMP	6.086	10.428	4.738	300.72	0.99	2.67	
LMFMP _{1.01}	6.085	10.423	4.739	300.61	1.00	2.73	
L _{1.03} MFMP _{1.01}	6.081	10.417	4.735	299.97	0.96	2.67	

 $Table \ S1 \ {\rm Crystal} \ {\rm structure} \ {\rm parameters} \ {\rm of} \ {\rm the} \ {\rm four} \ {\rm samples}$

Samples	Mn	Fe	Mg				
LMFMP	83.94	15.05	1.40				
L _{1.03} MFMP _{1.01}	84.19	14.64	1.71				

Table S2 Content of elements for LMFMP and $L_{1.03}MFMP_{1.01}$. (The test results are converted into molar ratios.)

No.	0.1 C	0.2 C	0.5 C	1 C	2 C	3 C	5C	10C	Ref.
This work	151.0	148.3	145.2	134.4	122.0	112.7	101.0	83.8	/
S1	138.0	131.0	125.0	119.0	109.0	/	89.5	/	[1]
S2	160.1	150.0	137.1	124.1	108.91	/	80.9	44.9	[2]
S 3	150.0	/	/	120.0	110.0	90.0	/	/	[3]
S4	139.0	/	105.0	89.0	/	/	69.0	56.0	[4]
S5	144.5	123.8	117.2	103.7	93.4	/	71.8	/	[5]

Table S3 The discharge capacity (m A h g⁻¹) of other literatures at different rates.

[1] Li R, Fan C, Zhang W, Tan M, Zeng T, Han S. Structure and performance of Na+ and Fe2+ co-doped Li1-xNaxMn0.8Fe0.2PO4/C nanocapsule synthesized by a simple solvothermal method for lithium ion batteries[J]. Ceramics International, 2019, 45(8): 10501-10510.<u>https://doi.org/10.1016/j.ceramint.2019.02.112</u>

[2] Zheng J, Yang J, Wu J, Li S, Wang M, Huang B, et al. Y3+ doping and electrochemical properties of LiFe0.5Mn0.5PO4@C cathode material for lithium-ion batteries[J]. Journal of Alloys and Compounds, 2023, 960.<u>https://doi.org/10.1016/j.jallcom.2023.170610</u>

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[4] El Khalfaouy R, Turan S, Rodriguez M A, Dermenci K B, Savacı U, Addaou A, et al. Solution combustion synthesis and electrochemical properties of yttrium-doped LiMnPO4/C cathode materials for lithium ion batteries[J]. Journal of Rare Earths, 2020, 38(9): 976-982.<u>https://doi.org/10.1016/j.jre.2019.06.004</u>

[5] Li C, Yu X, Liao C, Cui Z, Zhu J, Gao M, et al. Surface Modification Engineering Enabling LiMnxFe1-xPO4 Cathode Against Aggressive Cathode Chemistries for Excellent Performance Lithium-Ion Batteries[J]. ChemNanoMat, 2024, 10(4).<u>https://doi.org/10.1002/cnma.202300558</u>

Samples	R _{ct}	/ Ω	$D_{Li}^{+} / cm^2 s^{-1}$		
	Before cycling	After cycling	Before cycling	After cycling	
LMFMP	190.5	418.3	5.95×10 ⁻¹²	5.71×10 ⁻¹⁴	
L _{1.03} MFMP _{1.01}	76.34	191.8	1.67×10 ⁻¹¹	2.45×10 ⁻¹²	

Table S4 The values of R_{ct} and lithium ion diffusion coefficient before and after cycling.