Supplementary Information

Conformal CEI Formation Induced by Oxygen-Functionalized Conductive Agents on Mn-Rich Olivine Cathodes

Eunseo Ko[a,b,†], Seojin Lee[a,b,†], Jaehwan Kim[a,†], Minseo Kim[c,d], So Hee Kim[e], Yung-Eun Sung[c,d], Seung-Ho Yu[b*], Joonhee Moon[f*], Jungjin Park[a,g,h*]

[a] Energy Storage Research Center, Korea Institute of Science and Technology (KIST), Seoul, Republic of Korea, 02792

[b] Department of Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea, 02841

[c] School of Chemical and Biological Engineering, Seoul National University, 1, Gwanak-ro, Gwanak, Seoul 08826, Republic of Korea

[d] Center for Nanoparticle Research, Institute for Basic Science (IBS), 1, Gwanak-ro, Gwanak, Seoul 08826, Republic of Korea

[e] Advanced Analysis Center, Korea Institute of Science and Technology (KIST), Seoul, Republic of Korea, 02792

[f] Research Center for Materials Analysis, Korea Basic Science Institute, Daejeon, Republic of Korea, 34133

[g] Division of Energy & Environment Technology, Korea University of Science and Technology (UST), Seoul, Republic of Korea, 02792

[h] KHU-KIST Department of Converging Science and Technology, Kyung-Hee University (KHU), Seoul, Republic of Korea, 02447

† Authors contributed equally.

E-mail address: jpark716@kist.re.kr, junnymoon@kbsi.re.kr, seunghoyu@korea.ac.kr

Materials and methods

1. Synthesis of LMFP

$LiMn_{0.8}Fe_{0.2}PO_4$(LMFP) powder was synthesized via a solid-state reaction method. Lithium carbonate (Li_2CO_3, 99%, Sigma-Aldrich), manganese oxalate dihydrate ($MnC_2O_4 \cdot 2H_2O$, Mn 30%, Alfa Aesar), iron oxalate ($FeC_2O_4 \cdot 2H_2O$, 99%, Sigma-Aldrich), and ammonium phosphate dihydrate ($(NH_4)2HPO_4$, 98%, Sigma-Aldrich) were used as precursors. The precursors were thoroughly mixed and pulverized using a planetary ball mill (P2, Fritsch) at 300 rpm for 12 hours. The mixture was pelletized and subjected to the first sintering process in an Ar atmosphere at 600°C for 10 hours. Afterward, the pre-sintered material was mixed with D-(+)-glucose ($C_6H_{12}O_6$, 99.5%, Sigma-Aldrich) as a carbon source and underwent a second sintering process in an Ar atmosphere at 650 °C for 5 hours.

2. Preparation of LMFP Electrodes

The cathode was fabricated by combining LMFP powder, 5wt% solution of polyvinylidene fluoride (PVDF) and the respective conductive (SP, rGO) in a weight ratio of 90:03:07 in N-methyl-2-pyrrolidone (NMP, Daejung Chemicals & Metals Co., Korea). Reduced graphene oxide (rGO) was prepared by the mild oxidation of chopped graphite fibers using a modified Hummers' method, followed by heat treatment at 700°C. The rGO was premixed with a PVDF solution before being added to the slurry. Each slurry was mixed with a planetary centrifugal mixer (THINKY Co., Japan) and cast onto to the conductive carbon-coated aluminum foil (MTI Co., Korea) with a thickness of 300 μm followed by being dried in an oven at 40 °C.

The dried electrodes were punched into 11.3 mm-diameter (1.003 cm^2) using a punch tool (Wellcos Co., Korea)

For the cell configuration, the cathode was tested using a coin-type half cell (CR2032-type) with the addition of 100 μL of 1M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC)(1:1 vol%) (Dongwha Electrolyte Co., Korea) electrolyte and a polyethylene (PE, Celgard) separator.

3. Electrochemical measurements

Galvanostatic charge-discharge tests were performed at 60 °C using a battery testing system (Won-A Tech, WBCS3000L, South Korea). Long-term cyclability was evaluated at a constant current density of 0.5C (theoretical capacity of LMFP: 170 mAh g^{-1}) within the voltage range of 2.2–4.5 V (vs. Li/Li^+).

Electrochemical impedance spectroscopy (EIS) tests were conducted using a BioLogic potentiostat instrument (VMP3 BioLab, Inc.).

$$D_{Li} = \frac{R^2T^2}{2A^2n^4F^4c^2\sigma^2}$$

The following equation can be used to calculate the diffusion coefficient of the Li^+ (D_{Li})[1] :

R is the gas constant, T is the absolute temperature, A is the electrode area, n represents the electrons number, F is the Faraday constant, c is the lithium ion concentration, and σ shows the Warburg factor, which relates to Z′ through equation $Z' = R_{electrolyte} + R_{CEI} + R_{ct} + \sigma \cdot \omega^{-1/2}$. The σ can be obtained from the slope of Fig. S4. (b)

4. **Characterization**

Raman measurements were performed using a confocal Raman microscope (Ramanforce, Nanophoton, Japan) at the Korea Basic Science Institute (KBSI, QM12). A 532 nm laser with an excitation power of less than 1 mW was utilized. The crystalline silicon peak at 520 cm^{-1} served as an internal standard for system calibration. Raman spectra were collected using a 600 grooves mm^{-1} diffraction grating and a LU Plan Fluor 100× objective lens (Nikon, NA = 0.9), achieving a laser spot size of less than 1 μm^2 on the electrode surface. High-resolution transmission electron microscopy (HR-TEM) images of rGO and super P articles were obtained using transmission electron microscopy (FEI TecnaiF20 G2, Thermo Fisher Scientific, UK) at an acceleration voltage of 200 kV. X-ray diffraction (XRD) analysis of LMPF powder was performed with X-ray diffractometers (D8 advance, Bruker, USA) with Cu K-alpha beam source. The measurement was conducted over a 2θ range of 10–80° with a step size of 0.02°. The surface chemistry of cathode was analyzed using X-ray photoelectron spectroscopy (XPS, NEXSA, Thermo Fisher Scientific, UK) with a total of 10 scans, a spot size of 400 μm, and spectra acquired in constant analyzer energy (CAE) mode with a pass energy of 50.0 eV and

an energy step size of 0.10 eV. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis was performed using an instrument from PerkinElmer (USA). Prior to analysis, the powdered sample was completely dissolved in aqua regia, followed by a 100-fold dilution with deionized water. To ensure measurement reliability, each sample was analyzed in triplicate. The electrical resistivity of rGO and SP powders was measured using a four-point probe system (HANTECH Co., Ltd., Korea) equipped with a vertical compression cell comprising a cylindrical insulating mold (inner diameter: 22 mm) and copper plungers. Powder samples, pre-dried at 40 °C for 5 hours, were compressed up to 40 MPa using a universal testing machine. A constant current was applied through the outer electrodes, and the voltage drop was recorded between the inner electrodes using a precision source meter (RM3545, HIOKI, Japan). Resistivity (ρ) was calculated from the measured resistance (R = V/I) considering the cross-sectional area and compressed thickness. All measurements were performed at room temperature and repeated three times for reproducibility.

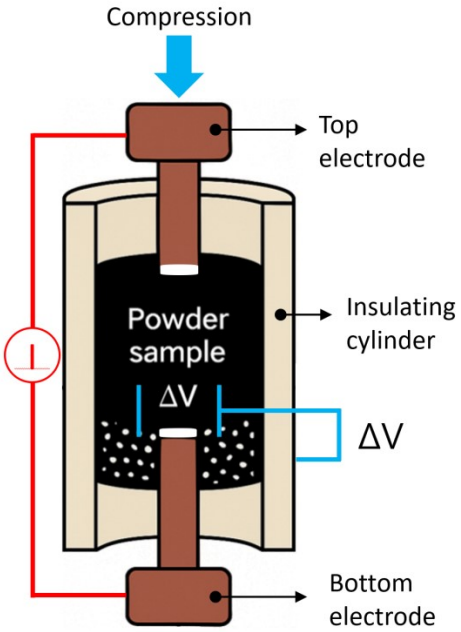


Fig. S1 Schematic illustration of a four-point probe measurement system under compression for powder resistivity analysis. Current (I) is applied via the top and bottom electrodes (in red), while the voltage drop (ΔV) is measured across two independent voltage-sensing probes embedded in the sample region (in blue). This configuration enables accurate determination of the powder's intrinsic resistivity by eliminating contact resistance effects during compression.

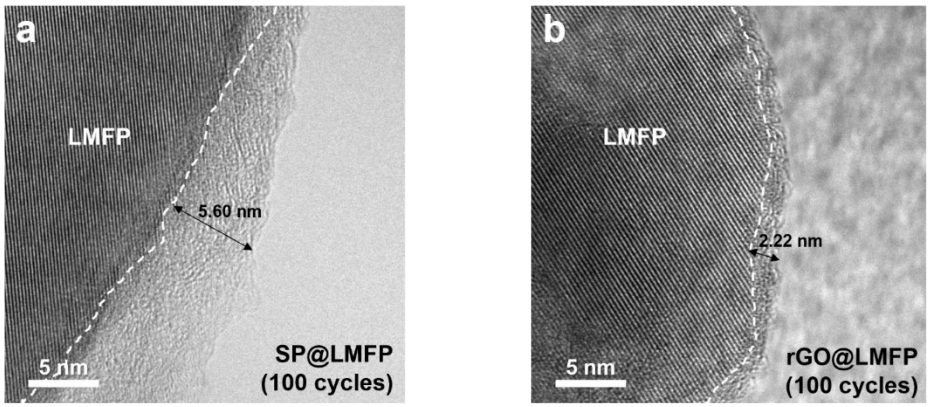


Fig. S2 TEM images of the CEI layers formed on the surface of (a) SP@LMFP and (b) rGO@LMFP electrodes after 100 cycles.

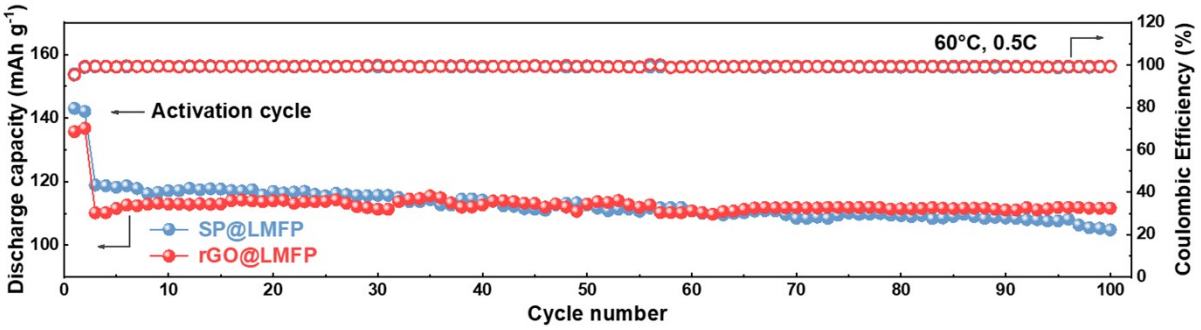
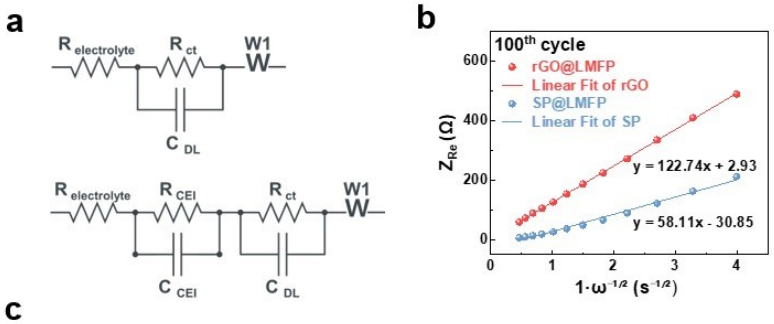


Fig. S3 Cycling performance based on actual discharge capacity: the initial two activation cycles were performed at 0.1 C, followed by cycling at 0.5 C.

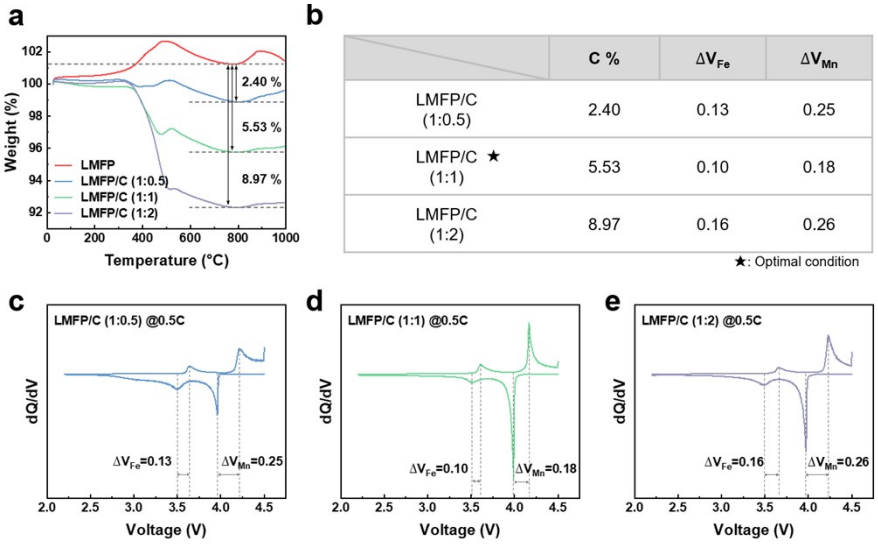


c

	$R_{electrolyte}$ [Ω]	R_{CEI} [Ω]	R_{ct} [Ω]	σ [Ω·s$^{-1/2}$]	D_{Li} [cm^2·s^{-1}]
rGO@LMFP (100 cycles)	1.46	13.25	111.90	122.74	4.63 x 10^{-15}
SP@LMFP (100 cycles)	1.05	24.42	22.01	58.11	2.04 x 10^{-14}

Fig. S4 (a) Equivalent circuit models corresponding to the pristine and 100th cycle samples. (b) Fitting of the real part of the impedance data against $\omega^{-1/2}$ to calculate the Warburg coefficient

σ' (c) Summary table of $R_{electrolyte}$, R_{CEI} , R_{ct} , σ and D_{Li} of rGO@LMFP and SP@LMFP after 100 cycles.



	C %	ΔV_{Fe}	ΔV_{Mn}
LMFP/C (1:0.5)	2.40	0.13	0.25
LMFP/C ★ (1:1)	5.53	0.10	0.18
LMFP/C (1:2)	8.97	0.16	0.26

★: Optimal condition

Fig. S5. (a) Thermogravimetric analysis (TGA) results, (b) summary table of TGA data and dQ/dV analysis, and dQ/dV profiles at 0.5C current density for LMFP samples with carbon coating ratios of (c) 1:0.5, (d) 1:1, and (e) 1:2.

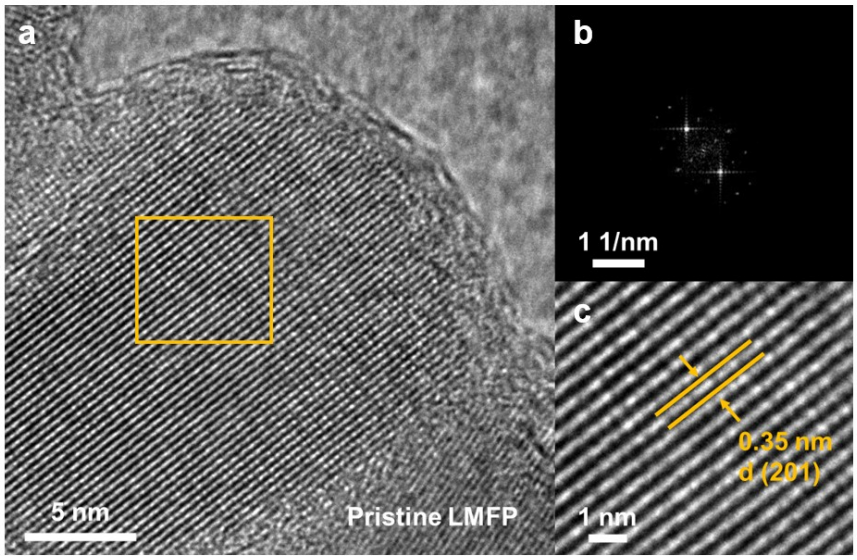


Fig. S6. (a) TEM image of the synthesized LMFP particles. (b) corresponding Fourier transform electron diffraction spot pattern. (c) high-magnification TEM image of the boxed region in (a).

Elements(/P)	Mn	Fe	P
Pristine LMFP	0.810	0.197	1.00
SP@LMFP (100 cycles)	0.721	0.209	1.00
rGO@LMFP (100 cycles)	0.788	0.204	1.00

Table S1. ICP-OES analysis showing Mn and Fe dissolution from SP@LMFP and rGO@LMFP electrodes after 100 cycles.

References

1. L. Wang, J. Zhao, X. He, J. Gao, J. Li, C. Wan and C. Jiang, Int. J. Electrochem. Sci., 2012, 7, 345–353.