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High-rate performance in a mixed olivine cathode with off-stoichiometric composition

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Electronic Supplementary Information

1. Synthesis: Li_2CO_3 (99%, Alfa Aesar), $FeC_2O_4{\cdot}2H_2O$ (99.999%, Alfa Aesar), $MnC_2O_4{\cdot}2H_2O$ (98%, Alfa Aesar), and $NH_4H_2PO_4$ (99%, Alfa Aesar) were carefully measured to be Li : transition metal : P ratios as 1 : 0.9 : 0.95 for the off-stoichiometric ($LiFe_{0.54}Mn_{0.36}P_{0.95}O_{4-\delta}$) composition and 1 : 1 : 1 for the stoichiometric ($LiFe_{0.6}Mn_{0.4}PO_4$) compositions in an argon-filled glovebox. The each batch was dispersed into acetone, sealed in a polypropylene jar, and milled with zirconia balls at 300 rpm for 24 h. After drying, the each mixture was calcined at 350°C for 10 h under argon atmosphere and heat treated at 650°C for 10 h under argon atmosphere.

2. Characterization: A Rigaku RU300 X-ray diffractometer (Cu-Kα, 50 kV/250 mA) was utilized to identify the crystal structure, and lattice parameters were estimated from the obtained diffraction patterns by Rietveld refinement, as implemented by an X'Pert HighScore Plus software. Particle morphology was observed by an FEI Philips XL30 field emission gun environmental scanning electron microscope (FEG E-SEM). The SEM samples were coated by Au-Pd to avoid charging. Particle substructure and composition were revealed by a JEOL 2010F analytical electron microscope via high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). The HRTEM and STEM images were obtained under an accelerating voltage of 200 keV, and the specimens were suspended on a copper grid with lacey carbon. For EELS, a 1 nm STEM probe of 9.6 mrad semiconvergence angle with a step size of 0.99 nm at 0.5 s exposure time per spectrum and 0.5 eV per channel energy dispersion was utilized along with the EELS detector (8.2 mrad semicollection angle) and the ADF detector (51.5 mrad inner radius). EELS

quantification was performed by using a signal integration window of 50 eV, Hartree-Slater model of partial ionization cross section, and power law background subtraction.

3. Electrochemistry: 80% active material, 15% carbon black (Timcal), and 5% polytetrafluoroethylene (PTFE, Dupont) were mixed and rolled to fabricate a uniform cathode film, which was assembled with a Li foil (FMC) anode, polymer separator (Celgard), and 1M $LiPF_6$ dissolved in ethylene carbonate and dimethyl carbonate electrolyte (Techno-semichem) in a 2016 coin cell. The loading density of the cathode film is approximately 2 mg cm^{-2}. The cell was galvanostatically cycled at a specific rate from 4.7 to 2.5 V on a Maccor 4000 and relaxed for 1 min in between every charge and discharge. A 1C rate is based on the theoretical capacities of each cathode: 165 mA g^{-1} for $LiFe_{0.54}Mn_{0.36}P_{0.95}O_{4-\delta}$ and 170 mA g^{-1} for $LiFe_{0.6}Mn_{0.4}PO_4$, where the conventional *n*C notation stands for the theoretical amount of current per unit mass that leads to full discharge in 1/*n* hours. For a rate capability test, the cell was charged at C/5 and held at 4.7 V until the current drops to a C/100 level (the CCCV profile) to ensure a fully charged state prior to individual discharges at various rates. The discharge rates are C/5, 5C, 20C, 40C, 60C, and 100C. All tests were performed at room temperature.

4. Rietveld refinement

Table S1. Lattice parameters, lattice volumes, and crystallite sizes obtained from Rietveld refinement and fitting agreement indices for $LiFe_{0.54}Mn_{0.36}P_{0.95}O_{4-\delta}$ and $LiFe_{0.6}Mn_{0.4}PO_4$.

Nominal Composition	a (Å)	b (Å)	c (Å)	V (Å^3)	Crystallite size (Å)	R_p	R_{wp}	χ^2
$LiFe_{0.54}Mn_{0.36}P_{0.95}O_{4-\delta}$	10.3648(7)	6.0400(3)	4.7122(1)	295.0034	297.8	6.65	8.70	2.39
$LiFe_{0.6}Mn_{0.4}PO_4$	10.3672(7)	6.0407(4)	4.7138(8)	295.2115	291.3	6.67	8.91	2.41

Space group: Pnma (62), Radiation λ: 1.540598 Å (Cu-Kα),

Scale factor: 0.001965, Overall B: 1.074, U = 0.024867, V = 0.073195, W = 0.097847, Pseudo-Voigt fit

Atomic coordinates and site occupancy factors (SOF) were not refined. Wyckoff positions are 4a (Li), 4c (Fe, Mn, P, O1, and O2), and 8d (O3). The SOF for Fe and Mn were set as 0.6 and 0.4, respectively.

5. EELS quantification

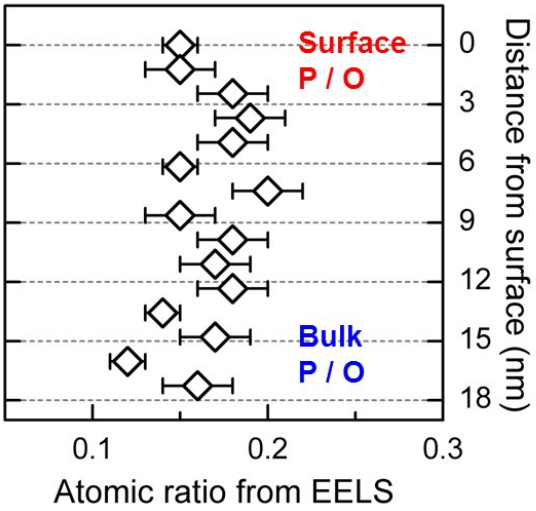

Figure S1. Atomic ratios of phosphorus to oxygen with respect to distance from surface obtained from EELS.

6. XPS

X-ray photoelectron spectra were collected on a PHI VersaProbe II XPS with a monochromatic Al (1486.6 eV) source. Pass energies were 187.85 eV for survey scans and 23.5 eV for high resolution scans. Data were processed by using a CasaXPS software and corrected with the C 1*s* binding energy of hydrocarbon at 284.8 eV. To fit a P 2*p* spectrum, peak position, FWHM, and area of $2p_{3/2}$ peak were first determined, and then $2p_{1/2}$ peak was set by shifting 0.85 eV from $2p_{3/2}$ with a fixed ratio of integrated intensity. Fitting results are summarized in Table S2.

Table S2. Results of fitted X-ray photoelectron spectra of P 2*p* binding energies for $LiFe_{0.54}Mn_{0.36}P_{0.95}O_{4-\delta}$ and $LiFe_{0.6}Mn_{0.4}PO_4$.

Samples	P $2p_{1/2}$	P $2p_{3/2}$	P $2p_{1/2}$ from $Li_4P_2O_7$	P $2p_{3/2}$ from $Li_4P_2O_7$	FWHM
$LiFe_{0.6}Mn_{0.4}PO_4$	134.09	133.23	-	-	1.31
$LiFe_{0.54}Mn_{0.36}P_{0.95}O_{4-\delta}$	134.09	133.23	134.53	133.68	1.27 / 1.19

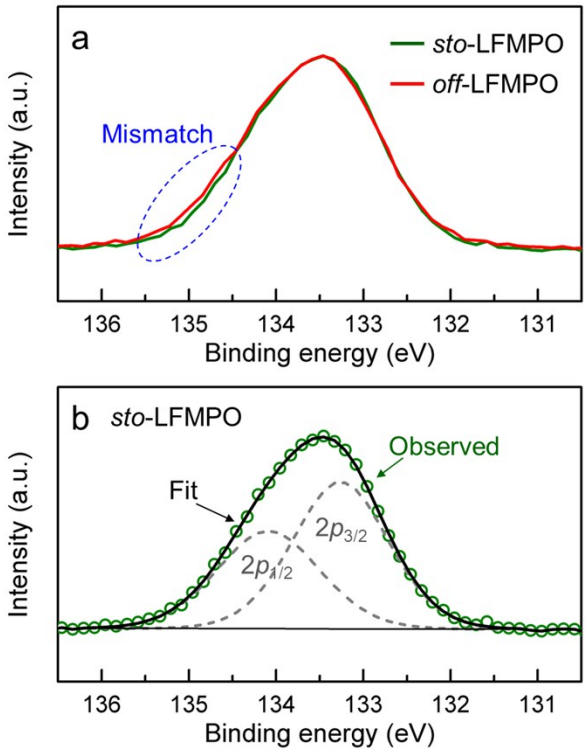

Figure S2. P 2*p* X-ray photoelectron spectra of (a) $LiFe_{0.6}Mn_{0.4}PO_4$ (*sto*-LFMPO) and $LiFe_{0.54}Mn_{0.36}P_{0.95}O_{4-\delta}$ (*off*-LFMPO) and (b) fitted spectrum of *sto*-LFMPO with P 2*p* doublet.