

Supplementary Material (ESI) for Chemical Communications
Electronic Supporting Information for the article:

**Mn Based Olivine Electrode Material with High Power
and Energy ****

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Experimental Section

Synthesis process

LiMnPO₄, LiFe_{0.1}Mn_{0.9}PO₄, and Li(FeCo)_{0.05}Mn_{0.9}PO₄ samples were prepared through the sol-gel synthesis. A stoichiometric amount of Li(CH₃COO)·2H₂O, Mn(CH₃COO)₂, Fe(CH₃COO)₂, Co(CH₃COO)₂·4H₂O, and NH₄H₂PO₄ precursors were dissolved in a container containing deionized(DI) water with glycolic acid and HNO₃ in order to perfectly create the sol state. This solution was heated to 70°C for making the dried gel state. Next, this precursor was fired at 350°C under Ar condition for 3hours. The mixture was then re-ground and manually pelletized using a disk-shaped mold. After pre-heating, we calcined the pellet at 520°C under Ar condition for 3hours.

Characterization

For the electrochemical characterization, the active materials were dry ball-milled with 20wt% Carbon black(Super-P) for 24 hours. The slurry of 80wt% carbon-coated LiMnPO₄, LiFe_{0.1}Mn_{0.9}PO₄, or Li(FeCo)_{0.05}Mn_{0.9}PO₄, 11wt% carbon black(Super-P), and 9wt% polyvinylidene fluoride dispersed in N-methyl-2-pyrrolidone(NMP) was prepared and cast on aluminum foil. NMP was evaporated at 70°C for 12 hours. Electrochemical cells were assembled into a CR2016 type coin-cell with a Li counter electrode, separator(Celgard 2400), and 1M LiPF₆ electrolyte in a mixture of 1:1 ethyl carbonate/dimethyl carbonate in an Ar-filled glove box. The charge/discharge test was carried out between 2.0V and 4.8V with various current rates from C/5 to 3C using a potentio-galvanostat(WonA Tech). Cyclic voltammetry was performed between 3.2V and 4.8V with a scan rate of 0.1mV s⁻¹. The partially lithiated samples were prepared by carefully retrieving the electrode from coin-cells at different discharge states. The electrodes were washed with dimethyl carbonate and dried

in a vacuum before being used in X-ray diffraction(XRD) study.

The XRD patterns were recorded using a Rigaku D/MAX-RC diffractometer that was equipped with Cu-K α radiation by step scanning($0.01^\circ \text{ s}^{-1}$) in the 2θ range of 15-45°. Structural refinements were performed by the Rietveld method using the General Structure Analysis System(GSAS). The morphology and particle size parameters were observed by field emission scanning electron microscopy(FESEM, PHILIPS XL30SFEG) and field emission transmission electron microscopy(FETEM, PHILIPS Tecnai F20).

The TEM sample preparation

For the TEM sample preparation of the charged particles, first, we made an electrochemical cell which was assembled into a CR2016 type coin-cell with an active material [working electrode], Li metal [counter electrode], a separator, and an electrolyte. And then, we charged the electrochemical cell by a galvanostat. After charging upto 4.0V, the charged coin cell was disassembled, the charged active material was separated from the cell, and then washed by dimethyl carbonate to remove salts in the electrolyte in an Ar-filled glove box. The charged active material was dispersed in the iso-propanol in an Ar-filled vial by sonication. In order to minimize the sample contamination by air exposure, the TEM sample on Cu grid was prepared in the glove box and transferred in the vial filled with Ar. Just before the TEM measurement, we opened the vial and then transferred the Cu grid onto TEM apparatus within 10 sec.

	a(Å)	b(Å)	c(Å)
LiMnPO ₄	6.115	10.463	4.754
LiFe _{0.1} Mn _{0.9} PO ₄	6.096	10.438	4.742
Li(FeCo) _{0.05} Mn _{0.9} PO ₄	6.088	10.426	4.739

Table S1. Lattice parameters of LiMnPO₄, Li(FeCo)_{0.05}Mn_{0.9}PO₄, and LiFe_{0.1}Mn_{0.9}PO₄.

Structural analysis

Crystallinity and Morphology

Before confirming the effect of Fe and Co doping into the Mn based olivine cathode, the presence of any impurities or second phases in the as-prepared material was investigated. The X-ray diffraction (XRD) patterns of LiMnPO_4 , $\text{LiFe}_{0.1}\text{Mn}_{0.9}\text{PO}_4$, and $\text{Li}(\text{FeCo})_{0.05}\text{Mn}_{0.9}\text{PO}_4$ are shown in the ESI†, Fig. S1. All materials show the standard diffraction peaks of the olivine *Pnma* space group, without any contamination or second phases. Variations in the three lattice parameters *a*, *b*, and *c* are tabulated in the ESI†, Table S1. The calculated lattice parameters of LiMnPO_4 clearly agree with previous reports.¹ The small differences of calculated lattice parameters among three materials are caused by the difference of ionic radii among high spin Mn^{2+} , Fe^{2+} , and Co^{2+} ($\text{Mn}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+}$). The systematic change of lattice parameters indicates that the Fe and Co are successfully incorporated in the structure. The morphologies of three materials are comparable, as shown in the ESI†, Fig. S2, which implies that the differences in electrochemical properties that originate from the morphologies of each particle will be negligible.

Structural change of $\text{Li}_{1-x}(\text{FeCo})_{0.05}\text{Mn}_{0.9}\text{PO}_4$

In order to investigate any possible changes of de/lithiation mechanism caused by the Fe and Co doping, an ex-situ XRD study was performed. The ESI†, Fig. S3 shows the XRD patterns of $\text{Li}_{1-x}(\text{FeCo})_{0.05}\text{Mn}_{0.9}\text{PO}_4$ at different voltage steps, ranging from 3.2 V to 4.8 V. Only conventional two-phase reactions, mainly occurring above ~ 4.2 V, were observed during charging. The noticeable change of XRD patterns does not appear below 4.2 V, despite the expected $\text{Fe}^{2+}/\text{Fe}^{3+}$ transition at ~ 3.4 V. It seems that the structural change from the possible local nucleation due to the small amount of Fe and Co in the matrix is too small to be

detected by the XRD measurement.

Reference

1. G. H. Li, H. Azuma and M. Tohda, *Electrochem. Solid-State Lett.*, 2002, **5**, A135–A137.

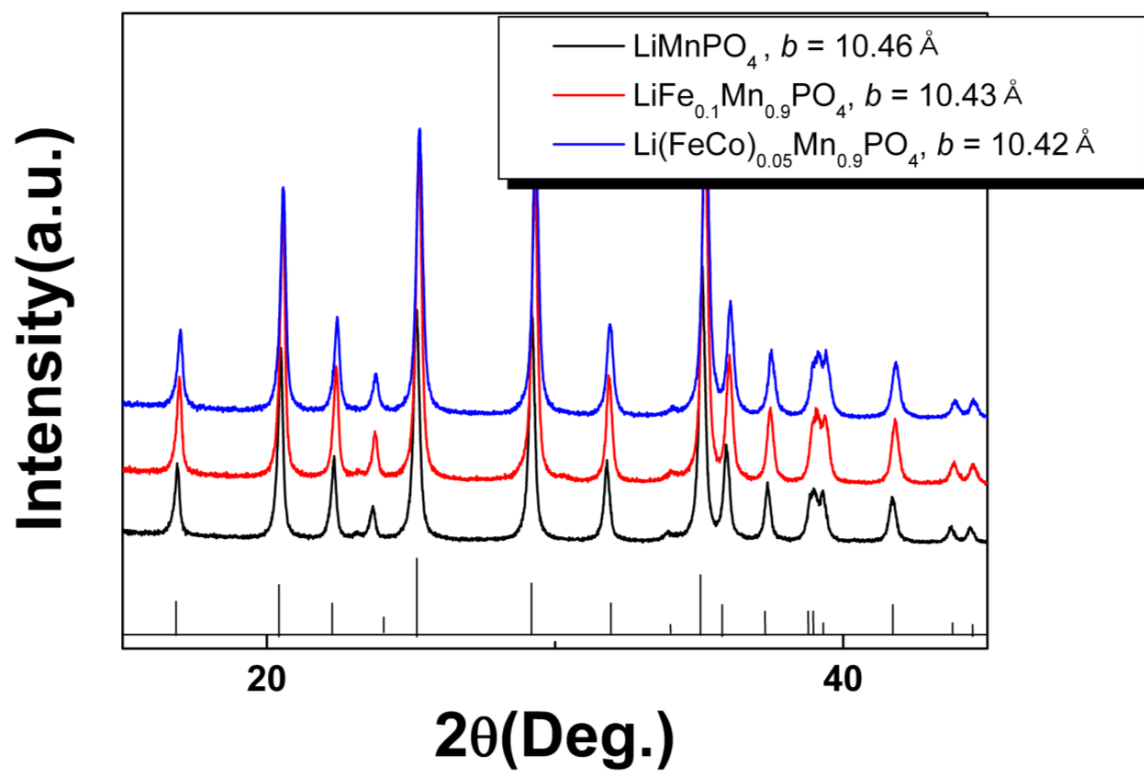


Fig. S1. XRD patterns of LiMnPO_4 , $\text{Li}(\text{FeCo})_{0.05}\text{Mn}_{0.9}\text{PO}_4$, and $\text{LiFe}_{0.1}\text{Mn}_{0.9}\text{PO}_4$.

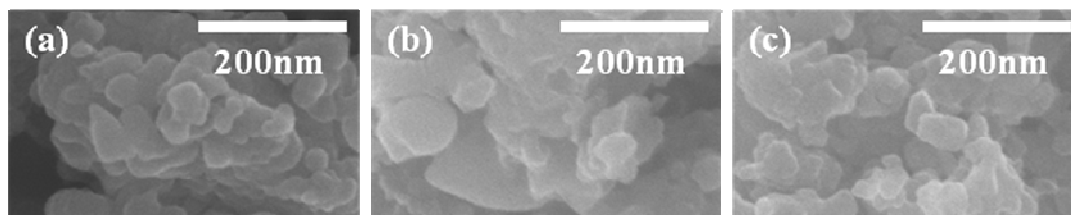


Fig. S2. SEM Images of (a) LiMnPO₄, (b) LiFe_{0.1}Mn_{0.9}PO₄, and (c) Li(FeCo)_{0.05}Mn_{0.9}PO₄.

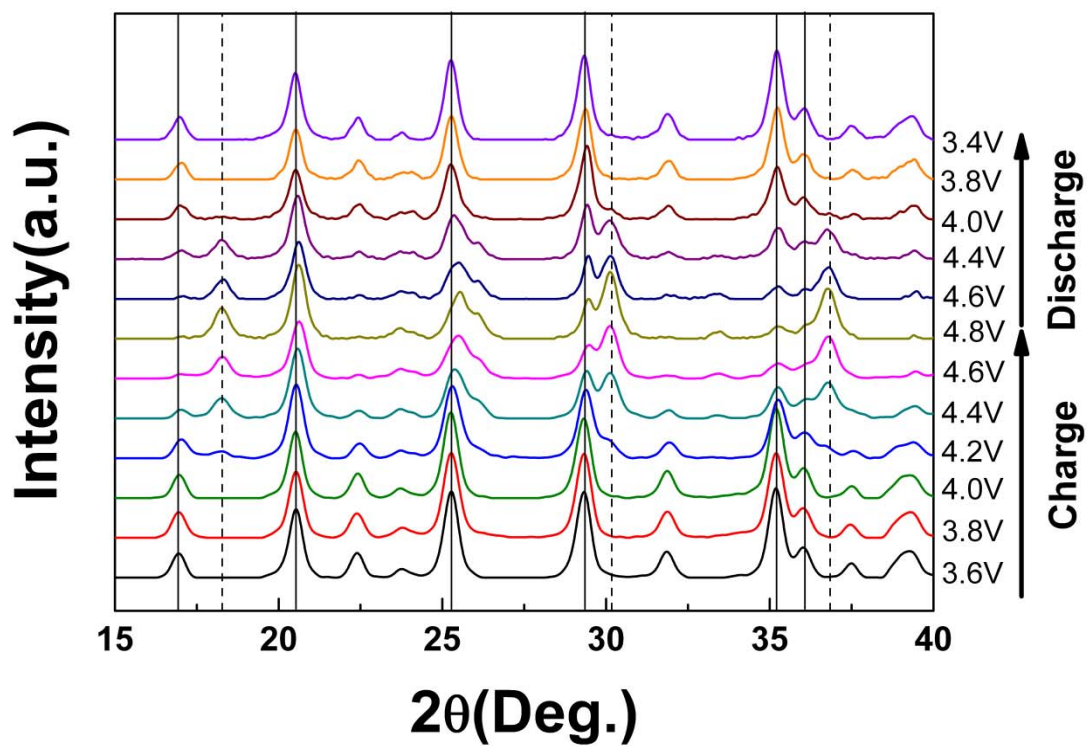


Fig. S3. *Ex-situ* XRD patterns of $\text{Li}_{1-x}(\text{FeCo})_{0.05}\text{Mn}_{0.9}\text{PO}_4$ between $2\theta = 15^\circ$ and $2\theta = 40^\circ$, at different charged states from 3.2V to 4.8V

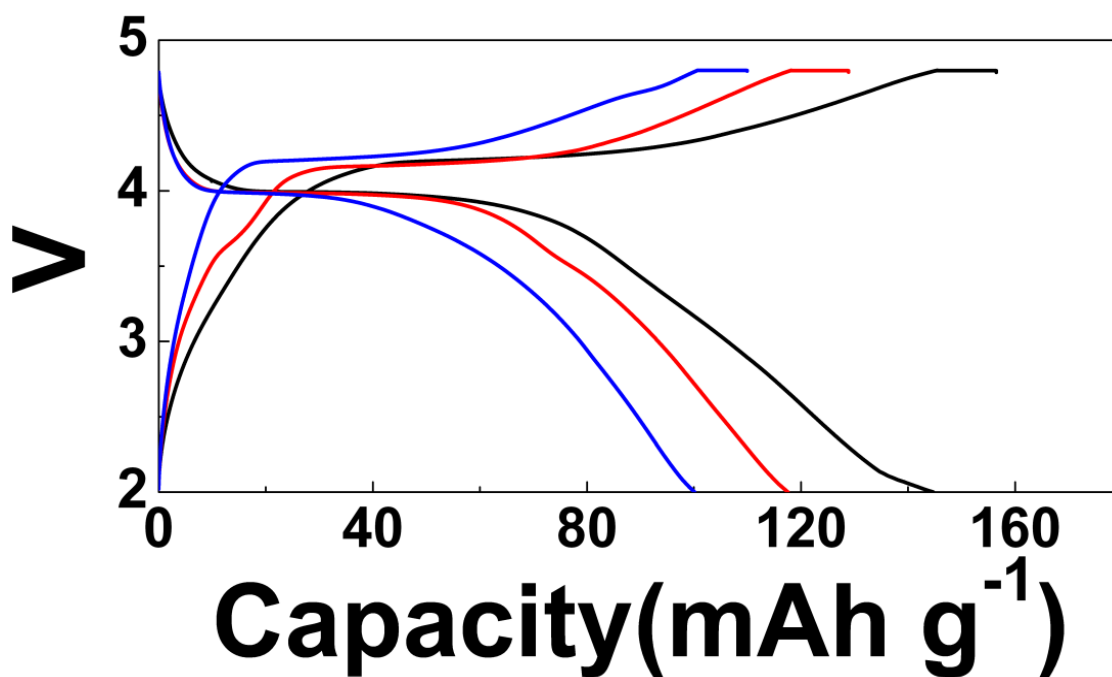


Fig. S4 One cycle charge/discharge curve of $\text{Li}(\text{FeCo})_{0.05}\text{Mn}_{0.9}\text{PO}_4$, $\text{LiFe}_{0.1}\text{Mn}_{0.9}\text{PO}_4$, and LiMnPO_4 at C/20.

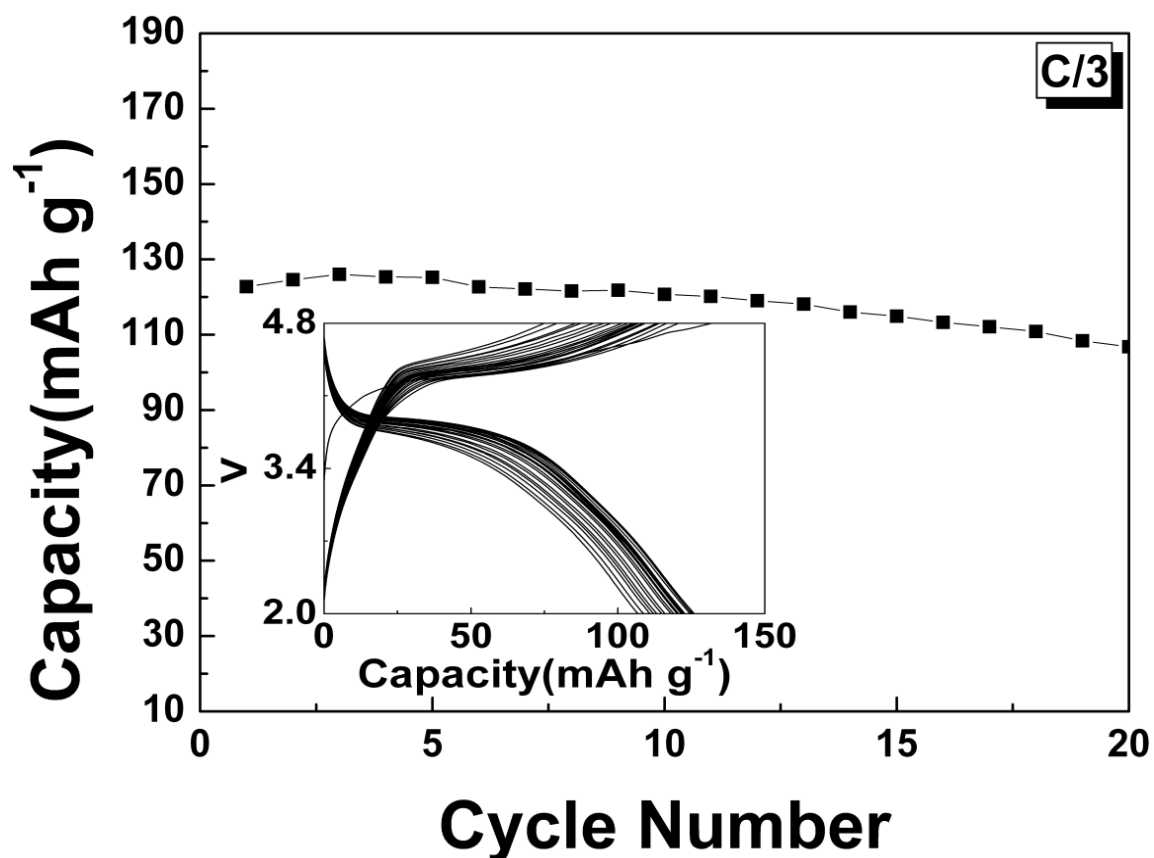


Fig. S5 Galvanostatic cycles of $\text{Li}(\text{FeCo})_{0.05}\text{Mn}_{0.9}\text{PO}_4$ at C/3. [1C = 170mA g^{-1}]

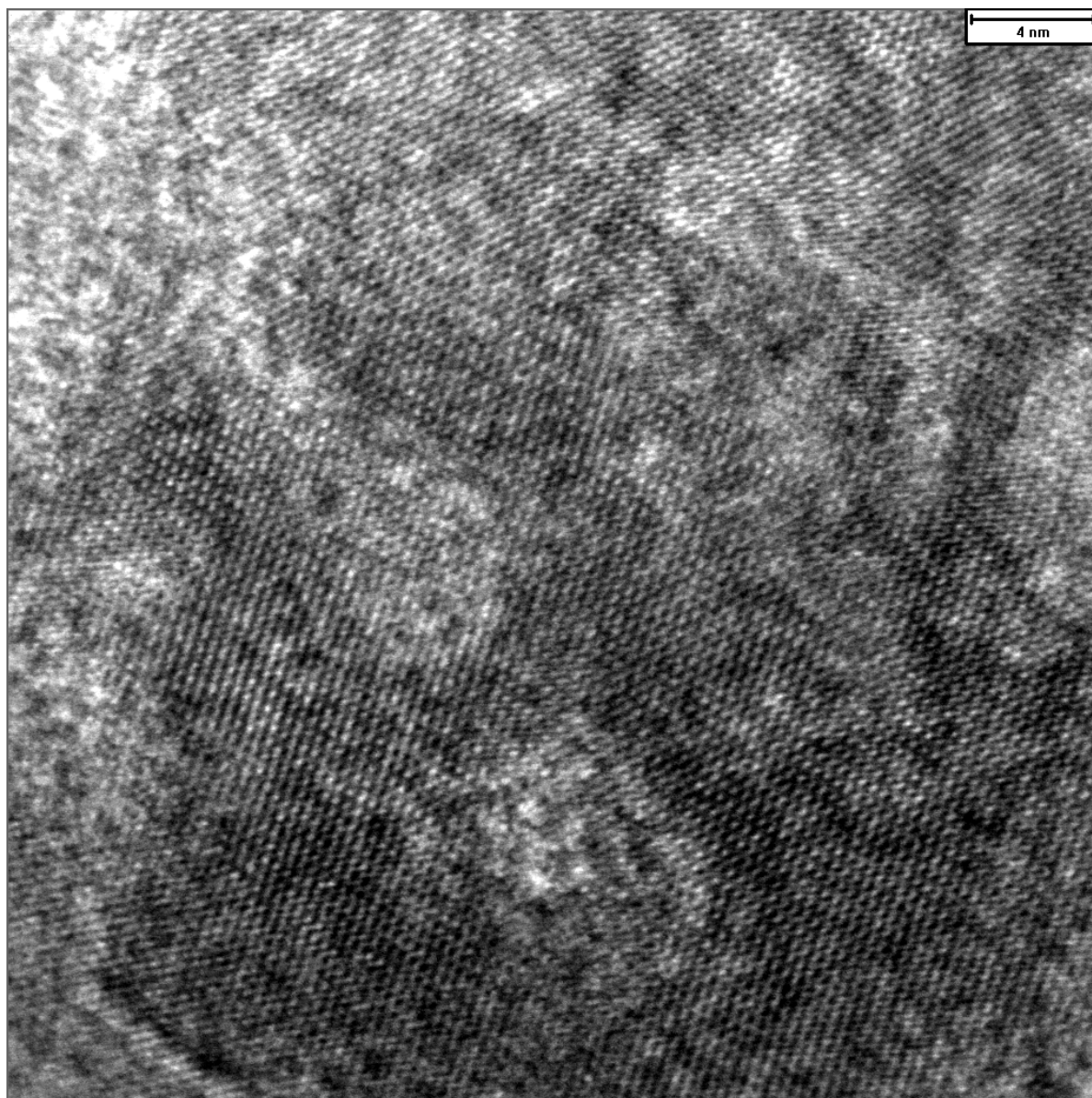


Fig. S6 The original HRTEM image of $\text{Li}(\text{FeCo})_{0.05}\text{Mn}_{0.9}\text{PO}_4$ after charging only below 4.0V