Supplementary Information

Modulation of Lithium Iron Phosphate Electrode Architecture by Magnetic Ordering for Lithium-Ion Batteries

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Experimental section

1. Electrode casting and pouch-cell fabrication

The positive electrode was prepared using a dispersion of $LiFePO_4$ (LFP, Johnson Matthey), Super P (TIMCAL), and polyvinylidene fluoride (PVdF, Solef-5130, Solvey) in *N*-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) at a *wt*. % of 90:5:5. The LFP electrodes were identically fabricated with 90:5:5 with LFP: flake graphite (TIMCAL, SFG-6) or Fe_3O_4 (Sigma Aldrich, 50-100 nm sized) : PVdF composition. The resulting slurry was cast on an Al foil and subjected to magnetic treatment with a neodymium magnet during drying. The cast electrode was pre-dried at 80 °C and dried under vacuum for 12 h at 120 °C before cell fabrication. The electrode was pressed to reach the electrode density with 2.0 g cm^{-3}. The negative electrode was composed of graphite (BTR), Super P (TIMCAL), styrene-butadiene rubber (SBR, Sigma-Aldrich), and carboxymethyl cellulose (CMC, Sigma-Aldrich) (SBR: CMC = 1:1 weight ratio) at a *wt*. % of 90:5:5. The water-based slurry was cast on a Cu foil and the coated electrode was pre-dried at 80 °C under vacuum for 12 h before cell assembly. A monolayered pouch cell was assembled with the positive electrode, polyethylene (PE) separator, and negative electrode. The cell had a negative to positive electrode capacity ratio (N/P ratio) of 1.08.

2. Electrochemical characterization of pouch cells

Electrochemical characterization of the graphite/LFP pouch cells was conducted. A blend of 1.0 M $LiPF_6$ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 = *v*/*v*) was injected to soak the electrode and separator into the electrolyte. Subsequently, the pouch cell was constructed after 24 h of aging in room temperature. The pouch cells were subjected to 0.1 *C* constant current (CC)-constant voltage (CV) cycles at a voltage range of 2.5–3.8 V at a cut off of 0.05 *C* using a galvanostatic cycler (TOYO, Japan). After cell formation, 1.0 *C* CC–CV charge (0.05 *C* cut-off) and 1.0 *C* discharge currents were applied to evaluate the cycle

performance. The direct current resistance (DC-*iR*) was measured by applying 2.5 *C* of current pulse with 1 min and 30 min of rest periods at an SOC of 50%. EIS was performed within the frequency range of 3.0 MHz–1.0 mHz using LFP/LFP symmetric cells with a 2032 coin-cell structure. The SOC of the charged pouch cells was 50% and the voltage amplitude was 5.0 mV. Galvanostatic intermittent titration technique was applied to compare the developed polarization at pristine and magnet-treated electrodes. The 10 min of 16 mA g^{-1} CC and 30 min of rest period was performed with lithiation step of the LFP electrodes. The polarization was calculated by subtracting closed-circuit voltages from quasi open-circuit voltages.

3. Morphology and surface analysis

Structural analysis of the electrode was conducted via X-ray microscopy (SKYSCAN 2214 CMOS). The surface composition of the cycled electrode was analyzed via XPS (ThermoFisher). The analyzed electrodes were disassembled in an Ar-filled glove box and washed with EMC solvents. The positive electrodes were examined via SEM (JEOL) after polishing their cross-sectional areas.

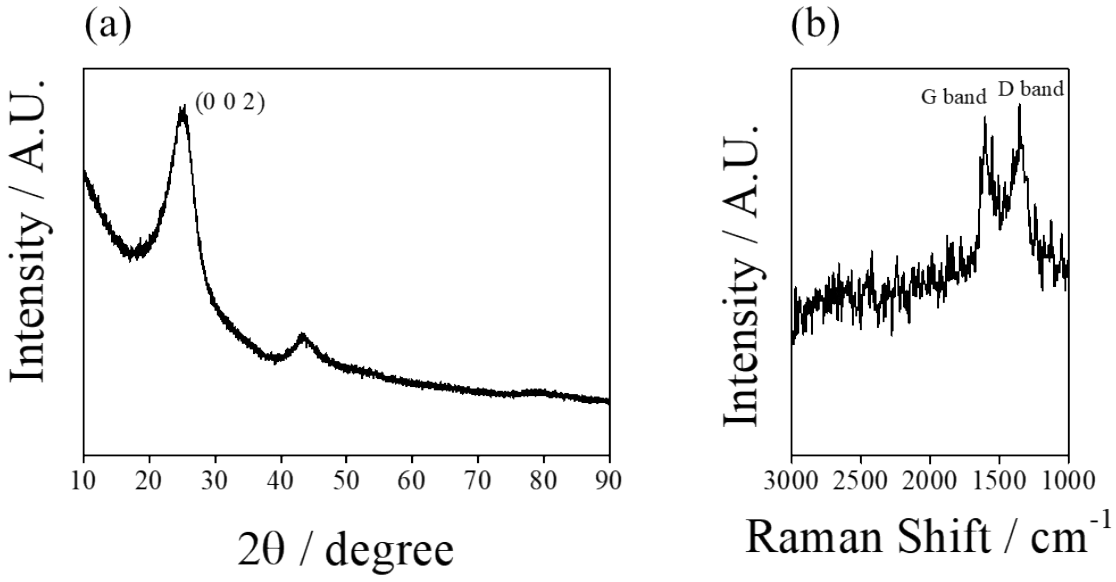

Figure S1 (a) XRD and (b) Raman spectrum obtained from the carbon additive

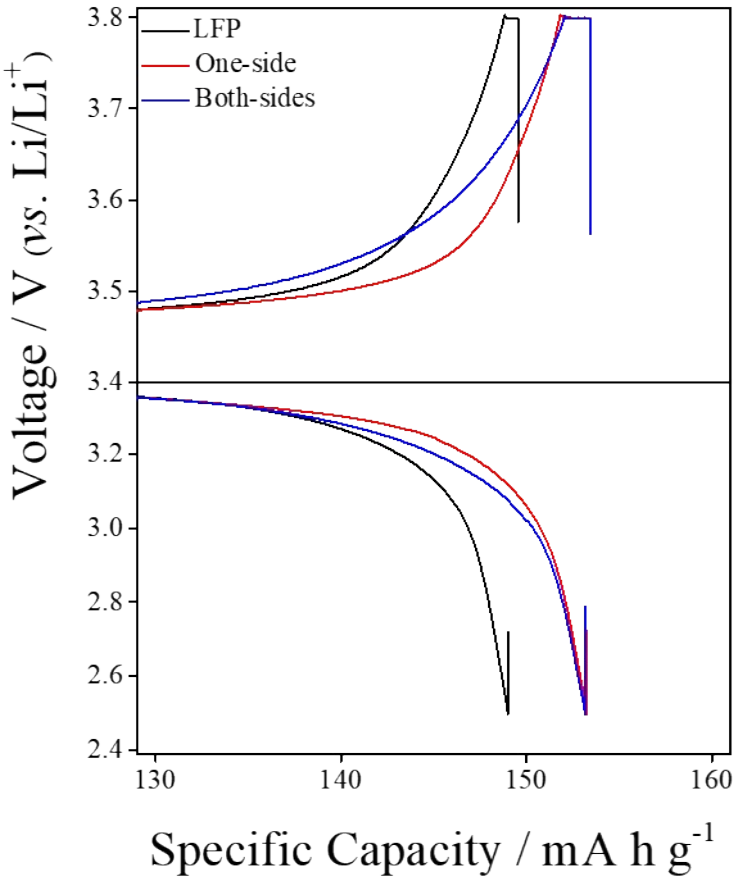

Figure S2 Voltage profiles from the Li/LFP cell with pristine, one-side and both-side magnet treated electrodes

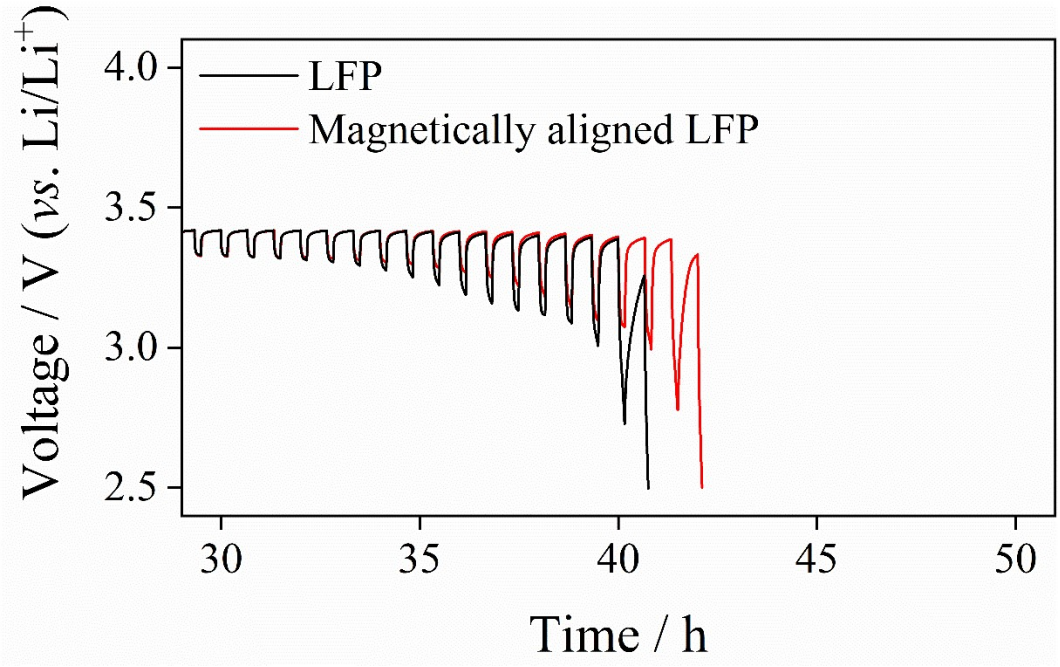

Figure S3. Time *versus* voltage curves obtained from the galvanostatic intermittent titration technique evaluation at Li/LFP coin cell

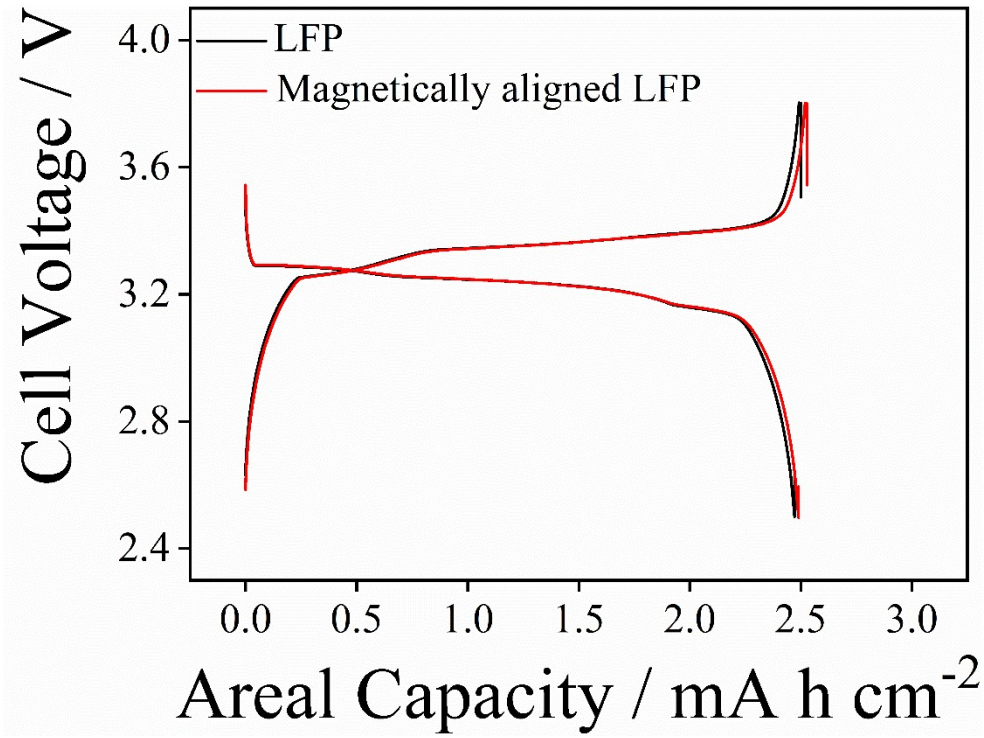

Figure S3 Voltage profiles from the graphite/LFP cell employing pristine and magnet treated LFP electrodes

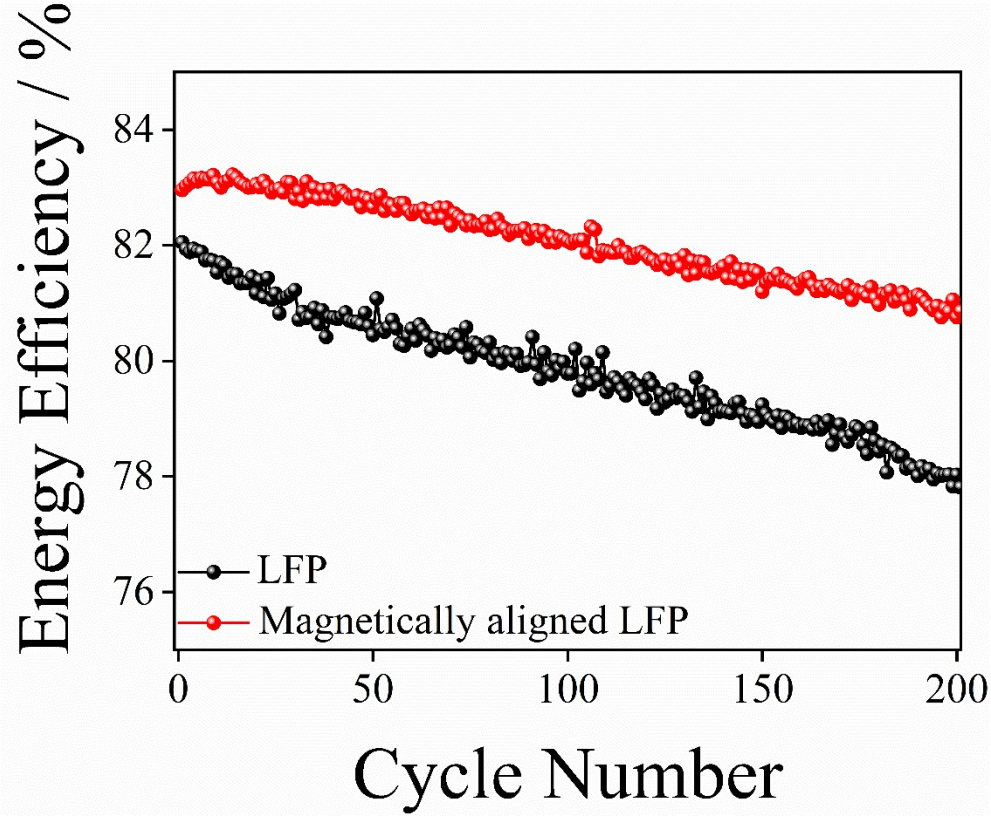

Figure S4 Energy efficiency obtained from the graphite/LFP cell with pristine and magnetically ordered LFP electrodes

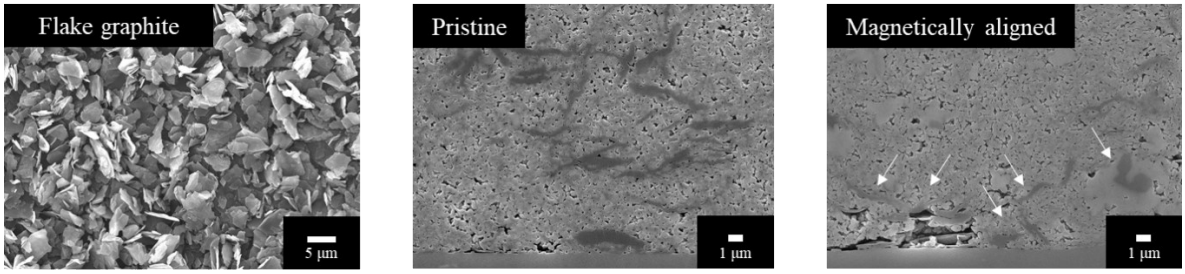

Figure S5. SEM images of flake graphite, pristine LFP electrode with flake graphite, and the magnetic field applied LFP electrode with flake graphite

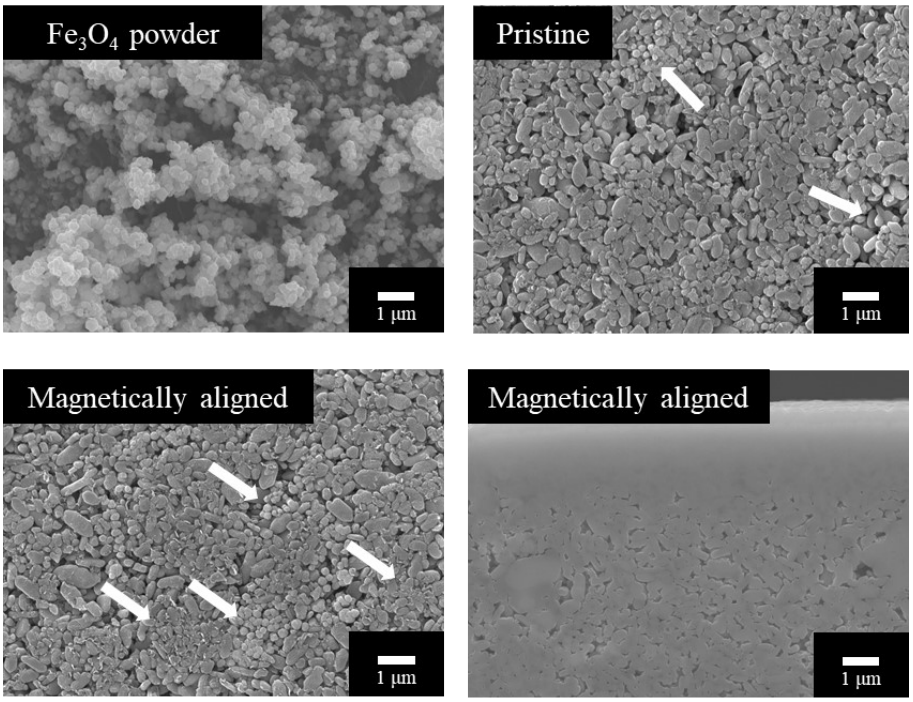

Figure S6. SEM images of applied Fe_3O_4 powder, pristine LFP electrode with Fe_3O_4, and the magnetic field applied LFP electrode with Fe_3O_4 at topmost and cross-section

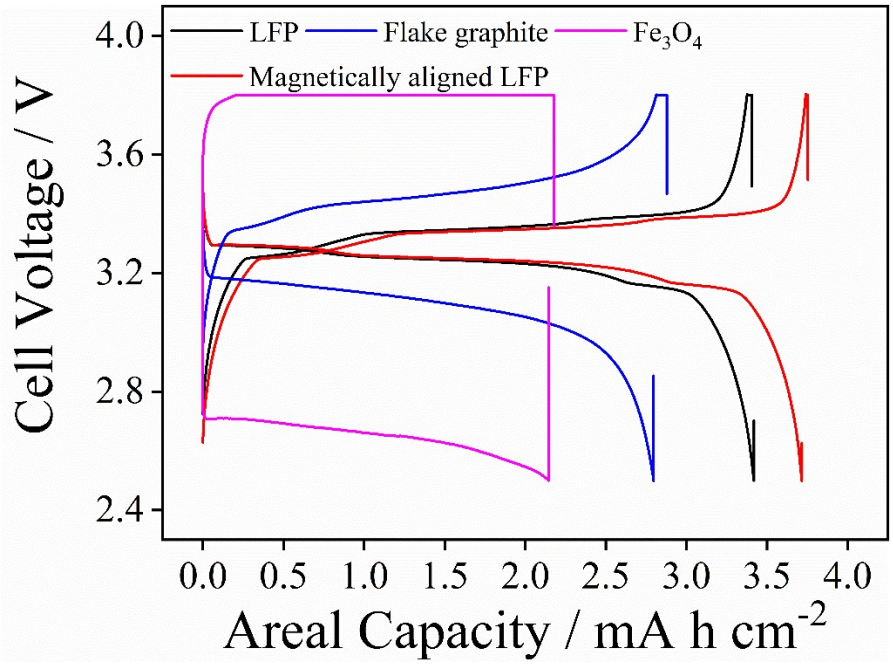

Figure S7. Initial formation voltage profiles obtained from the graphite/LFP pouch cells with differently designed electrodes.

Table S1. Design parameter of the evaluated graphite/LFP pouch cell

	Design parameter	**Value**
$LiFePO_4$ positive electrode	Discharge capacity	155 mA h g^{-1}
	Initial efficiency	99.9 %
	Active material ratio	90.0 %
	Mass loading	19.46 mg cm^{-2}
	Areal capacity	3.0 mA h cm^{-2}
	Electrode density	2.0 g cm^{-3}
Graphite negative electrode	Discharge capacity	332 mA h g^{-1}
	Initial efficiency	89.9%
	Active material ratio	90 %
	Mass loading	9.81 mg cm^{-2}
	Areal capacity	3.26 mA h cm^{-2}
	Electrode density	1.6 g cm^{-3}
Cell	NP ratio	1.08