SUPPLEMENTARY INFORMATION

Influence of pH-Induced Particle-Size Modulation on the Electrochemical Performance of Spinel $ZnFe_2O_4$ Anodes for Lithium-ion Batteries

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Galvanostatic intermittent titration technique (GITT) measurements were employed to investigate the Li^+ diffusion characteristics of the ZFO electrodes. These measurements were carried out after the electrodes completed five initial activation cycles to ensure stable electrochemical behavior. During the GITT process, intermittent current pulses with a current density of 100 mA g^{-1} were applied for 10 min, followed by an open-circuit relaxation period of 10 min to allow the cell potential to approach equilibrium. Prior to the GITT test, the cells were charged to 3.0 V, and subsequent discharge pulses were applied stepwise down to 0.01 V. The Li^+ diffusion coefficient (D) was extracted from the GITT measurements based on Fick's second law:[1-3]

$$D = \frac{4}{\pi}\left(\frac{iV_m}{FSZ_A}\right)^2\left[\frac{dE/d\delta}{dE/d\sqrt{\tau}}\right]^2 \qquad (S1)$$

Where: D represents the Li^+ diffusion coefficient ($cm^2\ s^{-1}$), i is the applied current (A), V_m is the molar volume of the electrode material ($cm^3\ mol^{-1}$), F is Faraday's constant, S is the apparent electrode area (cm^2), Z_A is the charge number, while $dE/d\delta$ is the slope of the steady-state coulometric titration curve, $dE/d\sqrt{\tau}$ denotes the slope of the linearized E-τ curve obtained during the applied current pulse of duration τ (s).

The **Eq. S1** can be further simplified as:

$$D = \frac{4}{\pi\tau}\left(\frac{n_m V_m}{S}\right)^2\left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \quad for\ \tau \ll \frac{L^2}{D} \qquad (S2)$$

Where: τ denotes the duration of the applied current pulse (s), n_m represents the number of moles (mol), ΔE_s refers to the steady-state voltage change induced by the current pulse, ΔE_t corresponds to the transient voltage variation observed during the constant-current pulse and L is the electrode thickness.

Table S1. Elemental ratio between Fe and Zn in three materials.

Samples	Ratio of Fe/Zn
ZFO_pH 10	2.39
ZFO_pH 11	2.25
ZFO_pH 12	2.11

Table S2. Ratio Fe^{3+}/Fe^{2+} and V_O/M-O in three materials by XPS analysis.

Samples	Ratio of Fe^{3+}/Fe^{2+}	Ratio of V_O/M-O
ZFO_pH 10	1.38	0.19
ZFO_pH 11	1.23	0.17
ZFO_pH 12	1.42	0.24

Table S3. Comparison of electrochemical performances of anodes related to Zn-, Fe-based oxides and commercial for LIBs (half-cell).

Material	Particle Size	Current density (A g^{-1})	Initial discharge capacity (mAh g^{-1})	Coulombic Efficiency in the first cycle (%)	Cycle lifetime/ End capacity (cycle/mAh g^{-1})	Ref.
$Zn_{0.5}Mg_{0.5}FeMnO_4$	Nanosized spherical (50-100 nm)	0.15	1132.9	60.2	80/300	[4]
Fe-doped ZnS-3 (FZC-3)	23 nm	0.2	1031.2	80.06	200/672	[5]
α-$Fe_2O_3/ZnFe_2O_4$	Micro-sized capsules	0.2	804.6	96	500/700	[6]
$ZnO/ZnFe_2O_4$ hybrid	Hybrid Nanostructures	0.2	998.4	70.6	200/704	[7]
$ZnFe_2O_4$/flake graphite	20-30 nm	0.1	848	87.7	100/730	[8]
$ZnFe_2O_4$ hollow	Microspheres (5-10 nm)	0.2	1152.2	71	120/1302	[9]
Commercial natural graphite (NG1.2)	Micro-sized (0.4-1.2 μm)	0.2	346.8	87.6	100/317.2	[10]
Spherical $Li_4Ti_5O_{12}$	0.5 μm	0.2	165	99.7	70/160	[11]
ZFO_pH 11	***37 nm***	***0.1***	***1270***	***77***	***60/932.2***	***This study***

Table S4. Resistances of ZFO electrodes.

	R_S (Ω)	R_{SEI} (Ω)	R_{CT} (Ω)
ZFO_pH 10	6.22	2.67	6.98
ZFO_pH 11	3.86	2.15	3.54
ZFO_pH 12	20.39	11.12	18.75

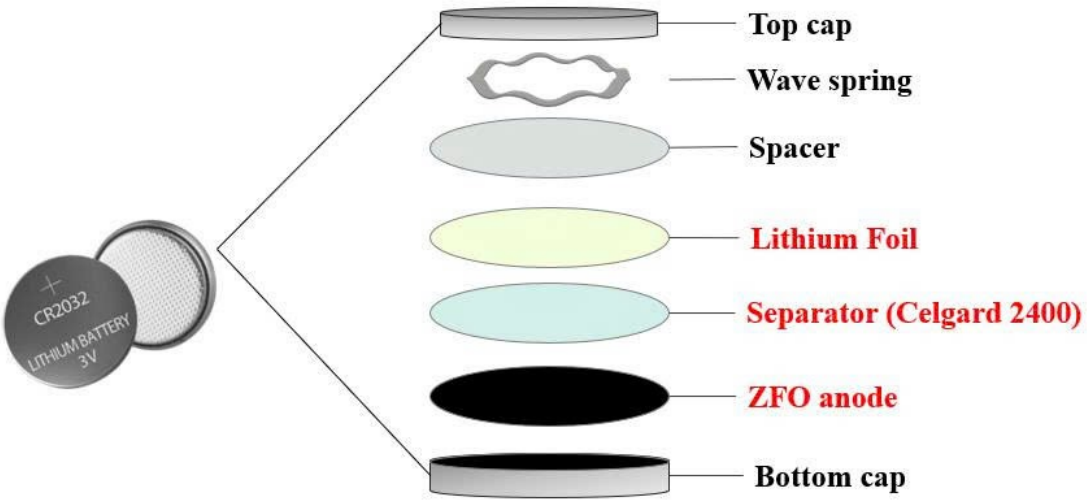

Fig. S1. Schematic illustration of the CR_2032 coin-type cell assembly.

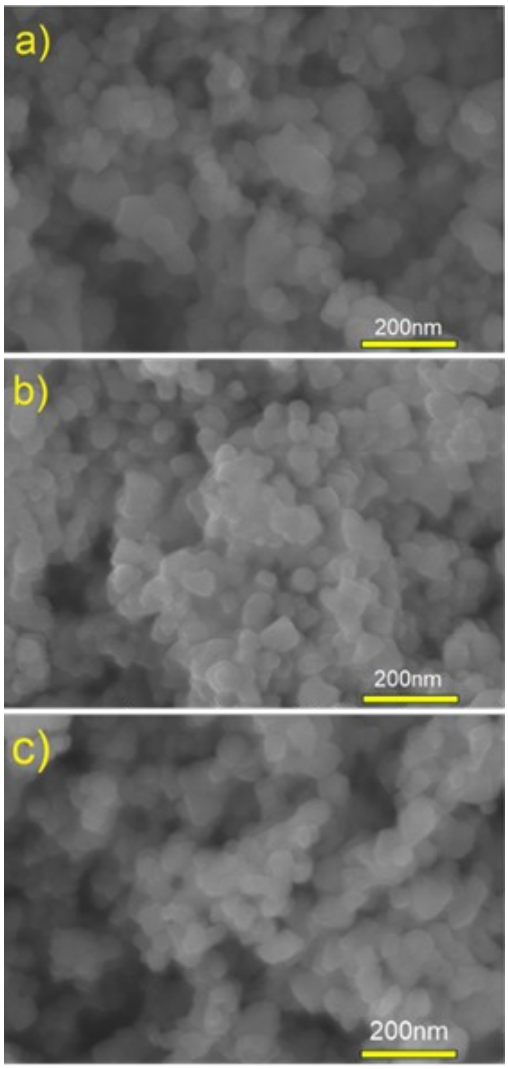

Fig. S2. (a-c) SEM images of ZFO_pH 10, ZFO_pH 11, and ZFO_pH 12 samples.

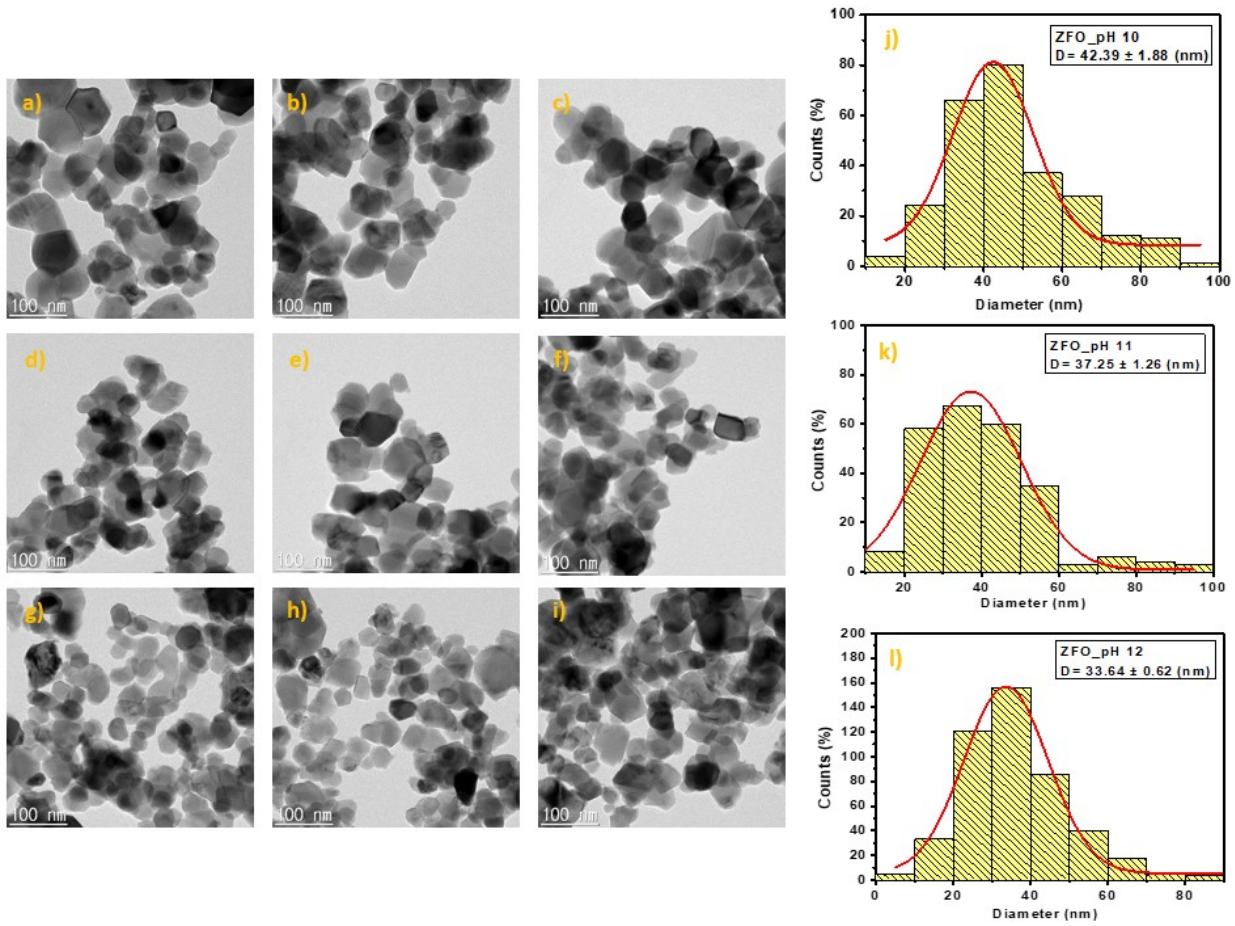

Fig. S3. Morphology and size distribution of the synthesized samples: (a–c) TEM images of ZFO_pH 10; (d–f) TEM images of ZFO_pH 11; (g–i) TEM images of ZFO_pH 12; and (j–l) the corresponding particle size distribution histograms of ZFO_pH 10, pH 11, and pH 12, respectively.

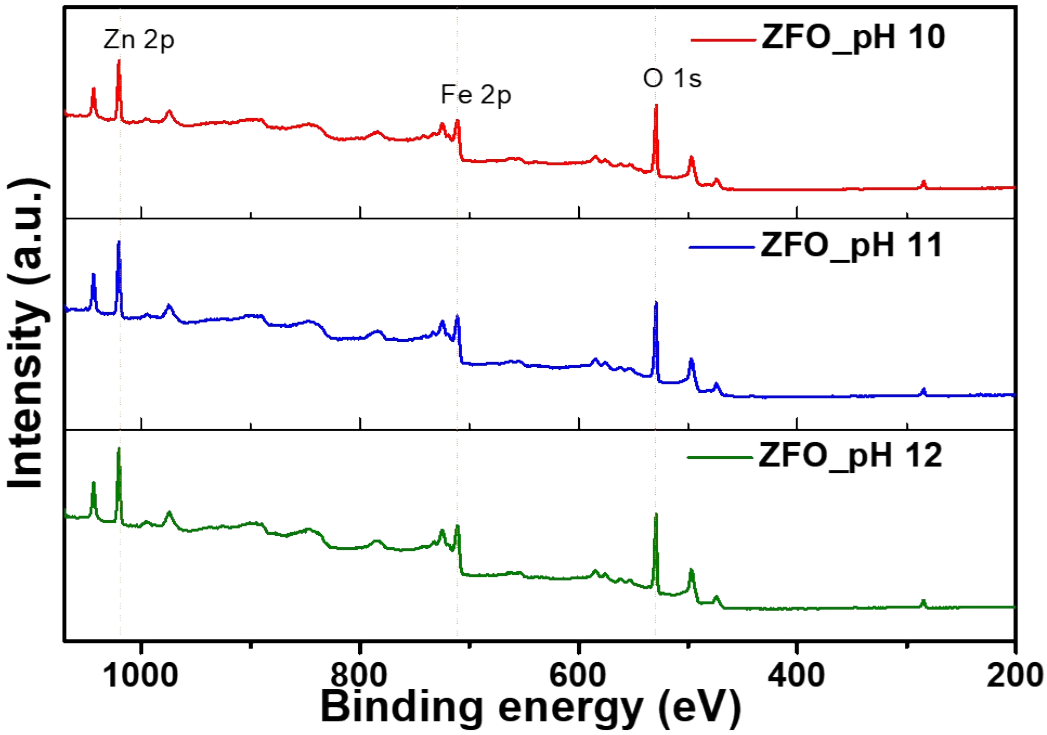

Fig. S4. XPS survey spectra for ZFO_pH 10, ZFO_pH 11, and ZFO_pH 12 samples.

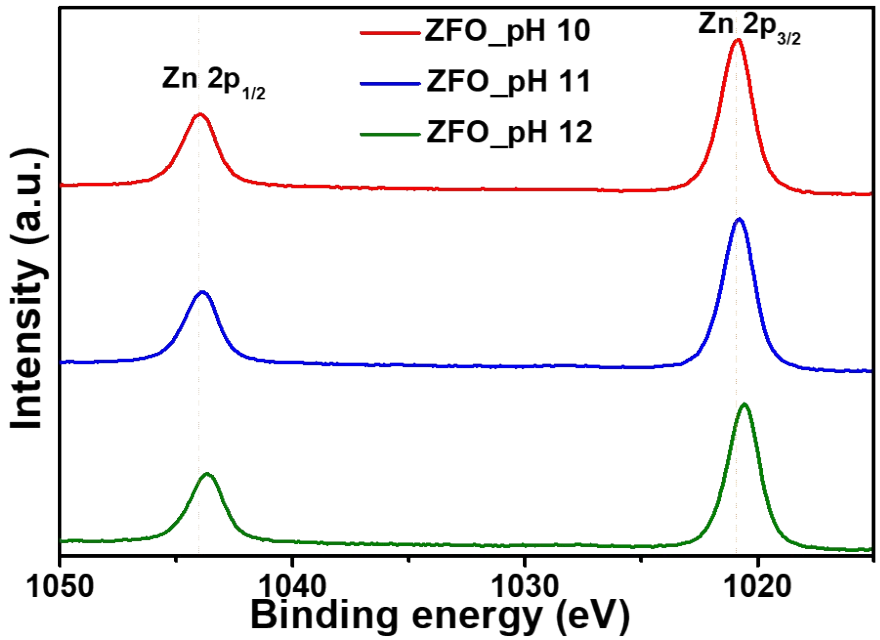

Fig. S5. High-resolution XPS spectra of Zn 2p for ZFO_pH 10, ZFO_pH 11, and ZFO_pH 12 samples.

References

1 E. Deiss, *Electrochim. Acta*, 2005, **50**, 2927-2932.

2 X. H. Rui, N. Ding, J. Liu, C. Li and C. H. Chen, *Electrochim. Acta*, 2010, **55**, 2384-2390.

3 Q. H. Nguyen, T. T. Salunkhe, T.-A. Nguyen, T. L. Nguyen and I. T. Kim, *Electrochim. Acta*, 2022, **436**, 141429.

4 Z. Chchiyai, O. El Ghali, A. Lahmar, J. Alami and B. Manoun, *Molecules*, 2023, **28**, 7010.

5 L. Zhang, Y. Zhang, Y. Han, L. Yang, G. Zou, H. Zhao, H. Hou and G. Gu, *Electrochim. Acta*, 2021, **399**, 139430.

6 W. Wu, Y. Wei, H. Chen, K. Wei, Z. Li, J. He, L. Deng, L. Yao and H. Yang, *J. Mater. Sci. Technol.*, 2021, **75**, 110-117.

7 D. Cai, H. Zhan and T. Wang, *Mater. Lett.*, 2017, **197**, 241-244.

8 L. Yao, X. Hou, S. Hu, X. Tang, X. Liu and Q. Ru, *J. Alloys Compd.*, 2014, **585**, 398-403.

9 H. Yue, S. Chen, W. Tie, L. Wu, W. Xie, T. Li, W. Li and H. Li, *Ionics*, 2021, **27**, 2835-2845.

10 Y.-J. Choi, Y.-S. Lee, J.-H. Kim and J.-S. Im, *Materials*, 2023, **16**, 6896.

11 H. Yan, Z. Zhu, D. Zhang, W. Li and Qilu, *J. Power Sources*, 2012, **219**, 45-51.