

Supporting Information

Rational Design and Synthesis of $\text{LiTi}_2(\text{PO}_4)_{3-x}\text{F}_x$ Anode Materials for High-Performance Aqueous Lithium Ion Batteries

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Synthesis Details of the $\text{LiTi}_2(\text{PO}_4)_{3-x}\text{F}_x$ ($x=0,0.06,0.12,0.18$) Samples

Firstly, CH_3COOLi , $\text{Ti}(\text{OBu})_4$, H_3PO_4 and citric acid were dissolved in absolute ethyl alcohol, respectively. Then, $\text{Ti}(\text{OBu})_4$, CH_3COOLi , H_3PO_4 solutions were slowly added into citric acid solution in sequence under continuous stirring. Stoichiometric LiF was finally added into the solution. After stirring for 4 h, a yellow homogeneous solution was formed. Several milliliters of water were added into the obtained solution to accelerate the hydrolysis of $\text{Ti}(\text{OBu})_4$ and generate a transparent gel. After evaporating the ethanol at 80 °C in water bath, the obtained dry gel was ground and heated in a tube furnace at 350 °C for 4 h under a flowing Ar atmosphere. The collected powder was reground and calcined at 750 °C for 15 h with a ramping rate of 5 °C min^{-1} under a flowing Ar atmosphere to obtain the final samples.

Preparation Details of Electrode for ARLBs

The LTP and LMO electrodes were made by a similar method. The electrodes were obtained by rolling the mixture of active material, activated carbon, Super P carbon and PTFE in a weight ratio of 70:10:10:10 into a film, which was then pressed onto a stainless steel mesh after drying at 120 °C for 12 h. The loading mass density of LTP electrode is 10~18 mg cm^{-2} , which is 2-5 times higher than previous reports. The mass ratio of LMO to LTP was 1.5~2. The Li_2SO_4 electrolyte was pre-treated by flowing argon injection into the solution to eliminate the soluble oxygen. Charge and discharge tests were conducted in the voltage window of 0.8-2.0 V on a Land automatic battery tester (Wuhan, China) at room temperature. The current density (A g^{-1}) or rate (C) is calculated based on the mass of anode active materials (including 11 % carbon content). The specific capacity (mAh g^{-1}), energy density (Wh Kg^{-1}), and power density (W Kg^{-1}) are based on the total mass of active electrode materials (anode + cathode).

The equivalent circuit of Nyquist plots

The intercept at the Z' axis in the high frequency range corresponds to the ohmic resistance (R_Ω), which presents the resistance of the electrolyte and electrode materials. The semicircle in the middle frequency range indicates the charge transfer resistance

(R_{ct}). The inclined line in the low frequency presents the Warburg impedance (W), which is associated with the diffusion of lithium ions in the solid matrix. A simplified equivalent circuit model has been constructed to analyze the impedance spectra. A constant phase element (CPE) represents the double layer capacitance.

The Calculation Method of Li^+ Diffusion Rate

$$D_{\text{Li}^+} = R^2 T^2 / 2A^2 n^4 F^4 C^2 \sigma^2 \quad (\text{s1})$$

$$Z' = R_e + R_{ct} + \sigma \omega^{-1/2} \quad (\text{s2})$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the anode, n is the number of electrons per molecule during oxidization, F is the Faraday constant, C is the concentration of Li^+ , σ is the Warburg factor which has a relationship with Z' as shown in Eq. (s2), R_e is the resistance between the electrolyte and electrode, R_{ct} is the charge transfer resistance, and ω is angle frequency. Figure 4c shows the relationship between Z' and square root of frequency ($\omega^{-1/2}$) in the low-frequency region. The slope of the linearly fitting lines of Z' and $\omega^{-1/2}$ is Warburg factor (σ). According to Eq. (s1), it is easy to calculate the diffusion coefficient of Li^+ (D_{Li^+}).

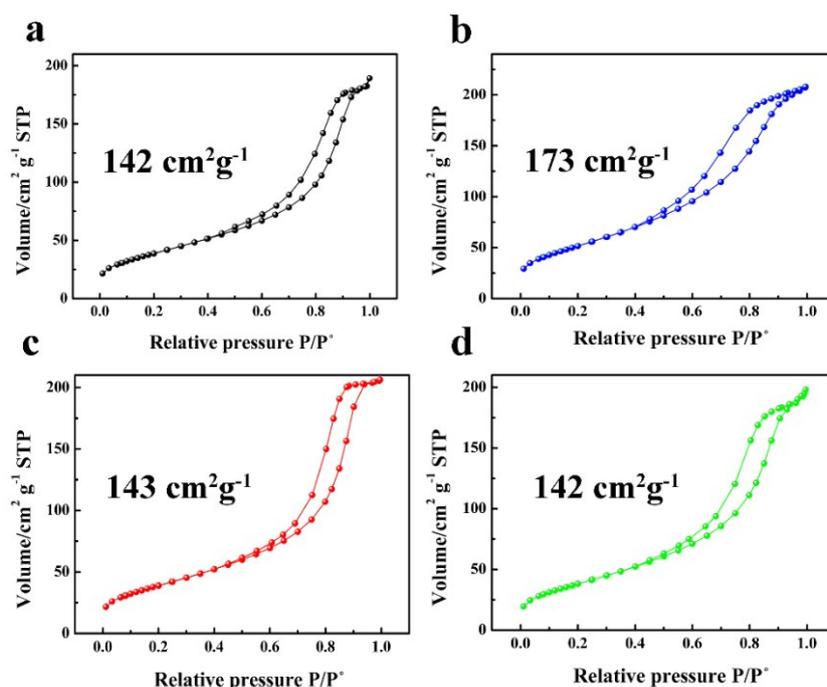


Figure S1. (a)-(d) Nitrogen adsorption-desorption isotherm of $\text{LiTi}_2(\text{PO}_4)_{3-x}\text{F}_x$ samples : (a) LTP, (b) LTP- $\text{F}_{0.06}$, (c) LTP- $\text{F}_{0.12}$, (d) LTP- $\text{F}_{0.18}$.

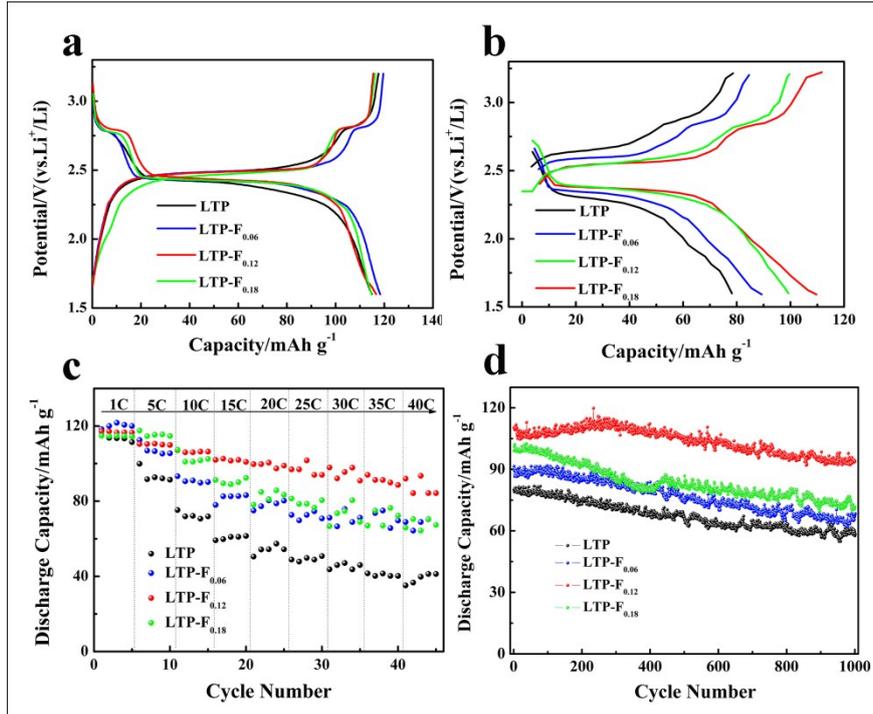


Figure S2. (a) Charge/discharge profiles of the $\text{LiTi}_2(\text{PO}_4)_{3-x}\text{F}_x$ samples at 1 C in organic half-cell; (b) Charge/discharge profiles at 10 C; (c) Discharge capacities from 1 C to 40 C; (d) Cycle performances at 10 C.

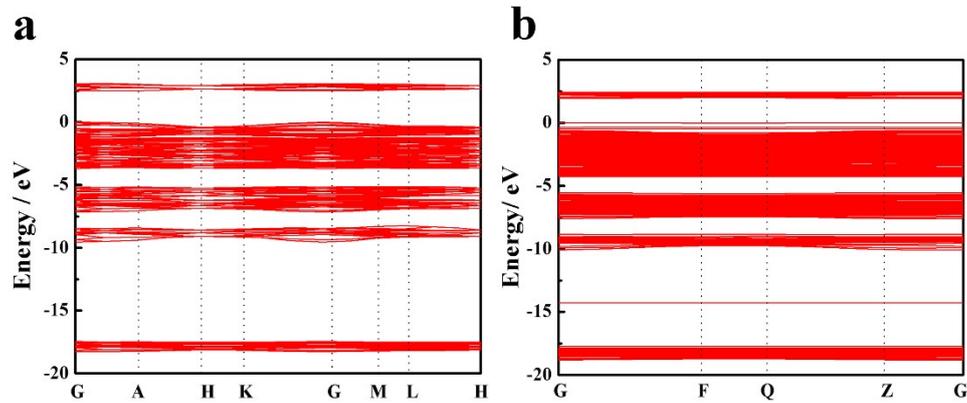


Figure S3. (a) Band structure of LTP; (b) Band structure of F-doped LTP. The band gap is 2.504 eV (for LTP) and 1.931 eV (for F-doped LTP), respectively.

Table S1. Structure parameters obtained from Rietveld refinement of XRD data for $\text{LiTi}_2(\text{PO}_4)_{3-x}\text{F}_x$

Sample	$a/\text{\AA}$	$c/\text{\AA}$	Cell volume/ \AA^3
LTP	8.5451	20.9153	1527.24
LTP-F _{0.06}	8.5427	20.9055	1525.63
LTP-F _{0.12}	8.5369	20.8888	1522.35
LTP-F _{0.18}	8.5034	20.76184	1501.24

Table S2. Kinetic parameters of $\text{LiTi}_2(\text{PO}_4)_{3-x}\text{F}_x$ samples

Sample	$R_{\text{ct}} (\Omega)$	σ	$D_{\text{Li}^+} (\text{cm}^2 \text{s}^{-1})/\text{EIS}$
LTP	150	12.08	1.26×10^{-12}
LTP-F _{0.06}	80	3.31	1.68×10^{-11}
LTP-F _{0.12}	35	3.51	1.49×10^{-11}
LTP-F _{0.18}	60	5.17	6.90×10^{-12}