Supplementary Information (SI) for Physical Chemistry Chemical Physics.

A molecular titration strategy: utilizing built-in electric field to detect lithium diffusion coefficient in $LiFePO_4$

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Experimental section

Materials

Potassium ferricyanide ($K_3[Fe(CN)_6]$) (SPAIN, 98%), Potassium ferrocyanide($K_4[Fe(CN)_6]$) (Shanghai Yuanye Biotechnology, 99.5%), $LiFePO_4$(Shanghai Dibai Biotechnology, 98%)

Preparation of titration solutions

Potassium ferricyanide ($K_3[Fe(CN)_6]$) is chosen in this study because it is an reversible, robustness and environmental friendly redox couple, which may ensure reproducibility of the test process. Specifically, 3.2924 g $K_3[Fe(CN)_6]$ was added to 100 mL deionized water to prepare 100 mL, 0.1 M $K_3[Fe(CN)_6]$ solution, 4.2239 g $K_4[Fe(CN)_6]$ also was added to 100 mL deionized water to prepare 100 mL, 0.1 M $K_4[Fe(CN)_6]$ solution. Subsequently, 1 mmol (0.157757 g) $LiFePO_4$ was added into to 25 ml $K_4[Fe(CN)_6]$ solution in a three electrode cell to establish a equilibrium state. To collect a series of potential change data, it is necessary to divide the titration process into multiple times. In other words, 0.1 M $K_3[Fe(CN)_6]$ solution was added into $LiFePO_4$ & $K_4[Fe(CN)_6]$ solution stepwise with volume of 0.5 mL for each titration. The added total amount of 0.1 M $K_3[Fe(CN)_6]$ solution at the end of the titration is 20 mL, corresponding 2.0 mmol.

X-ray diffraction (XRD) measurement

All the X-ray patterns were collected by D8 ADVANCE X-ray powder diffraction system with Cu(λ=0.154 nm) Co(λ=0.179 nm) beam under the accelerating voltage of 40 kV.

Scanning electron microscopy (SEM)

Morphology of $LiFePO_4$ was characterized with SEM (SU8010) at an accelerating voltage of

3 kV.

Brunauer Emmett Teller (BET) Test

The specific surface area (S) is measured with N_2 adsorption-desorption isotherms by BET method at 77K.

Construction of MTT system

MTT system mainly consists of working electrode, counter electrode and reference electrode. Here, we select Titanium plate as working and counter electrode for its excellent corrosion resistance and outstanding electrochemical performance, the reference electrode is Ag/AgCl. Moreover, the MTT system is put on a magnetic stirrer and a stir bar is put into MTT system to reduce concentration polarization and increase the reaction rate. The whole MTT system is displayed in Figure S8.

Open circuit potential monitoring

As we described in the main text, the decreasing value of the open circuit potential (OCP) is correlated with the amount of extracted Li^+ through Nernst equation, and the decreasing rate of the OCP is depend on the diffusion rate of Li^+ in the $LiFePO_4$ solid. If we can establish the formulation between decreasing rate of OCP and diffusion rate of Li^+ in $LiFePO_4$ solid, the diffusion coefficient of Li^+ in $LiFePO_4$ solid can be calculated out through this formulation. Therefore, the OCP decreasing trend need to be monitored. A Corrtest electrochemical workstation (CS310X-4) was used to monitor the decreasing rate of OCP.

Finite difference method (FDM) to calculation

The finite difference method (FDM) is a numerical method for solving differential equations by approximating the derivatives using finite difference approximations. It involves replacing the derivatives in the differential equation with algebraic expressions that approximate the rate of change of the function at discrete points in the domain. This method converts the differential equation into a system of algebraic equations, which can then be solved to obtain an approximate solution to the original differential equation. Therefore, FDM method is used to calculate the numerical value of $\frac{dE}{d\sqrt{t}}$. The software is MATLAB package.

Supporting figures

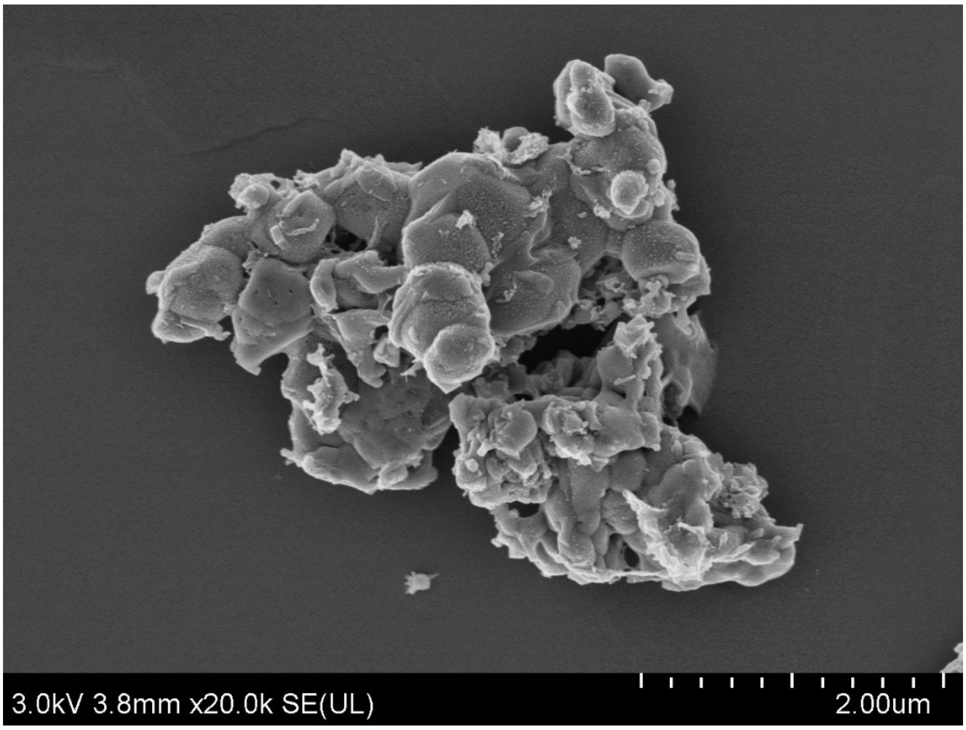

Figure S1. Scanning electronic microscopy (SEM) of $LiFePO_4$ material

BET Report

BET surface area	Correlation coefficient	Molecular –sectional area
12.7543m^2	**0.9999938**	**0.1620nm^2**

Figure S2. The BET test results of $LiFePO_4$ material

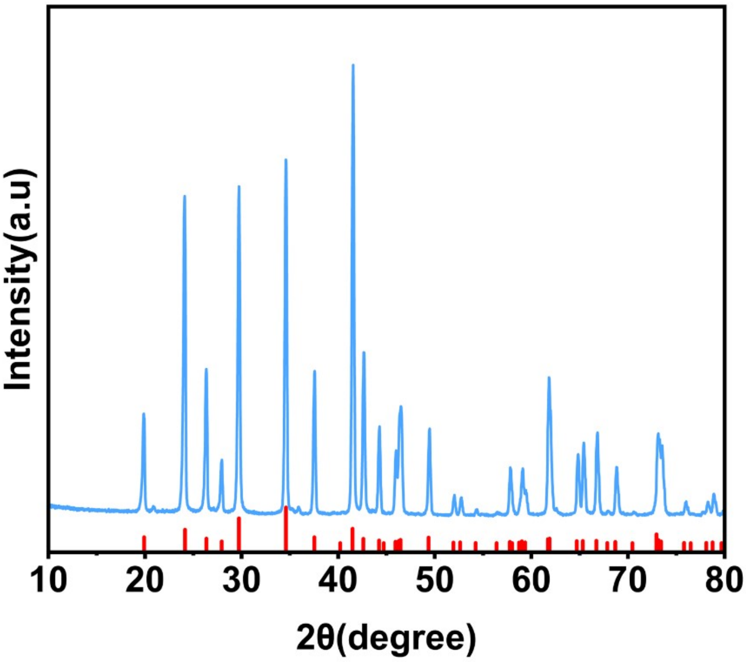

Figure S3. X-ray diffraction patterns of $LiFePO_4$ powder

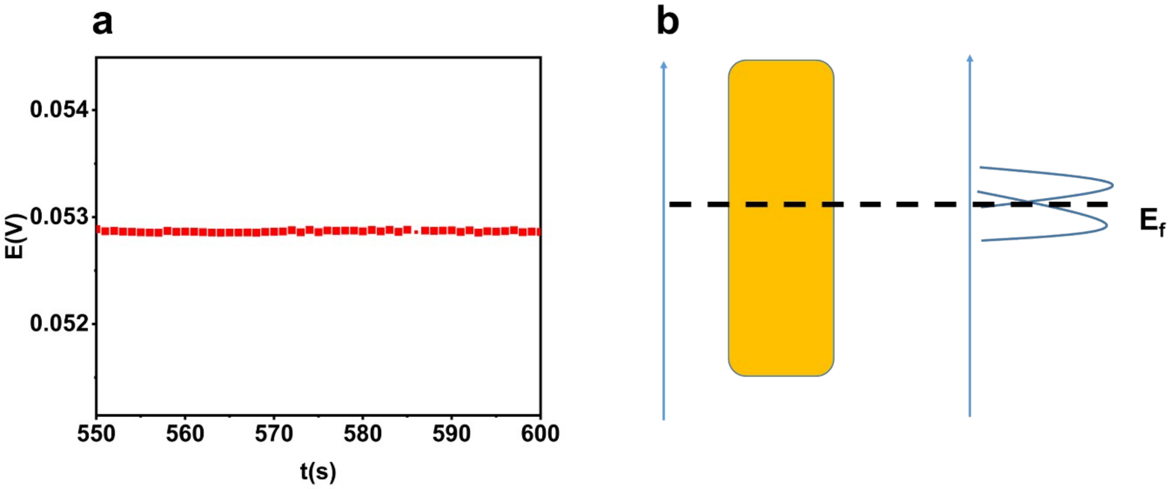

Figure S4. The system potential after adding $LiFePO_4$ into $K_4Fe[(CN)]_6$ solution. (a) The open circuit potential (OCP). (b) The schematic of Fermi level energy after reaching to equilibrium state.

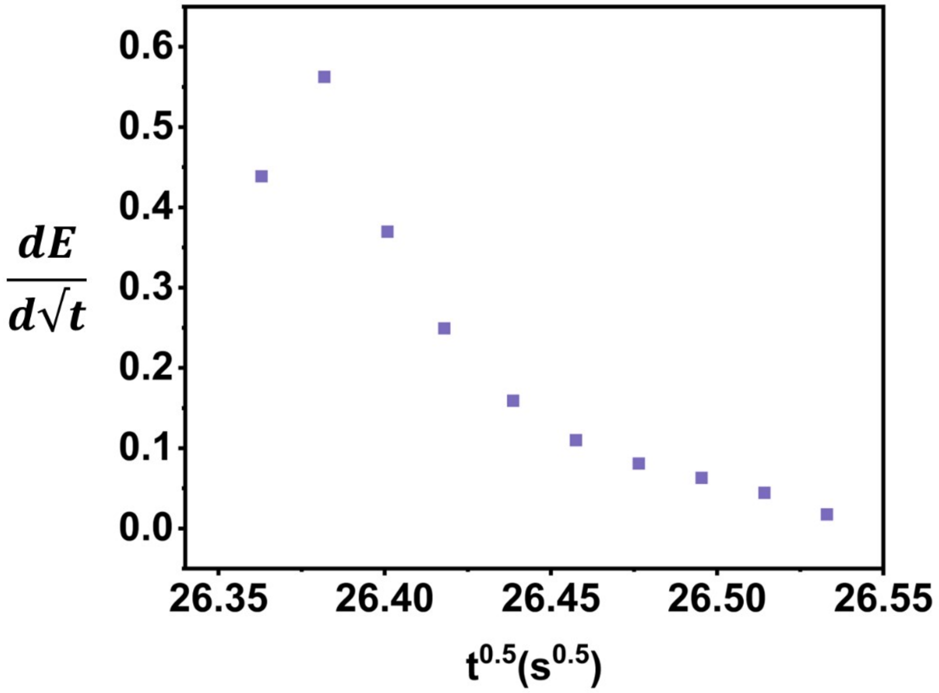

Figure S5. The value of $\frac{dE}{d\sqrt{t}}$ at different $t^{0.5}$, the figure indicates that $\frac{dE}{d\sqrt{t}}$ is a variable depended on $\sqrt{t}$.

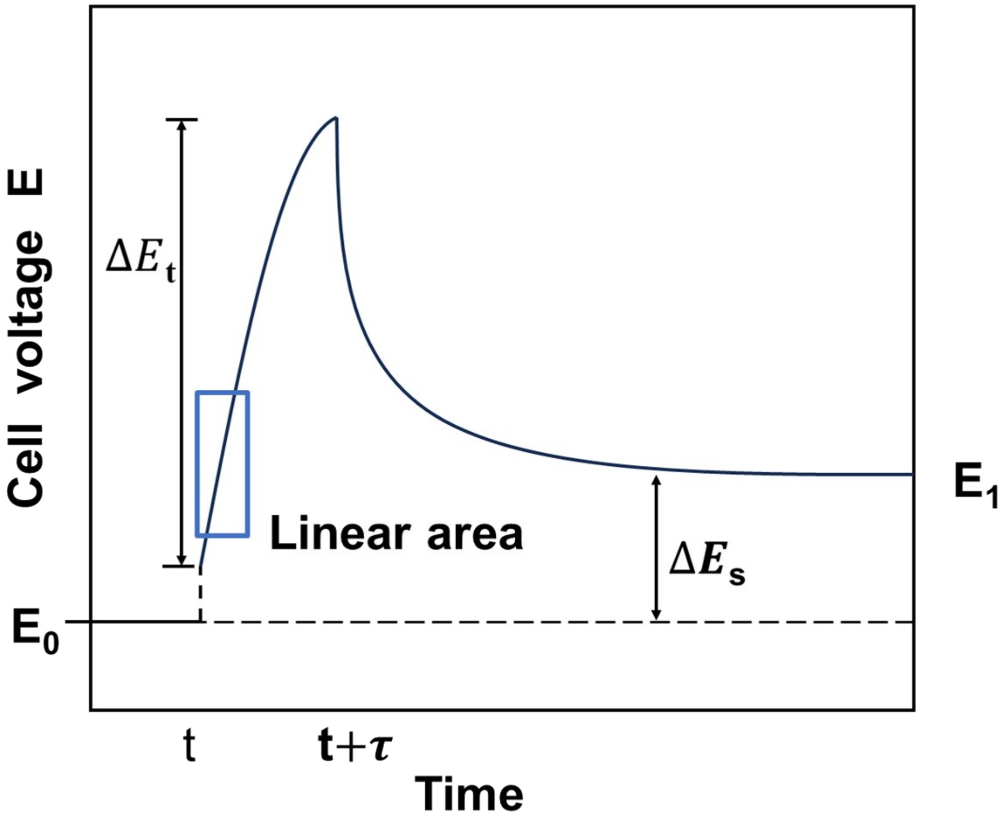

Figure S6. The $\frac{dE}{d\sqrt{t}}$ obtained from the linear area in GITT. In the linear area, the $\frac{dE}{d\sqrt{t}}$ value can be obtained from the most fitted data.

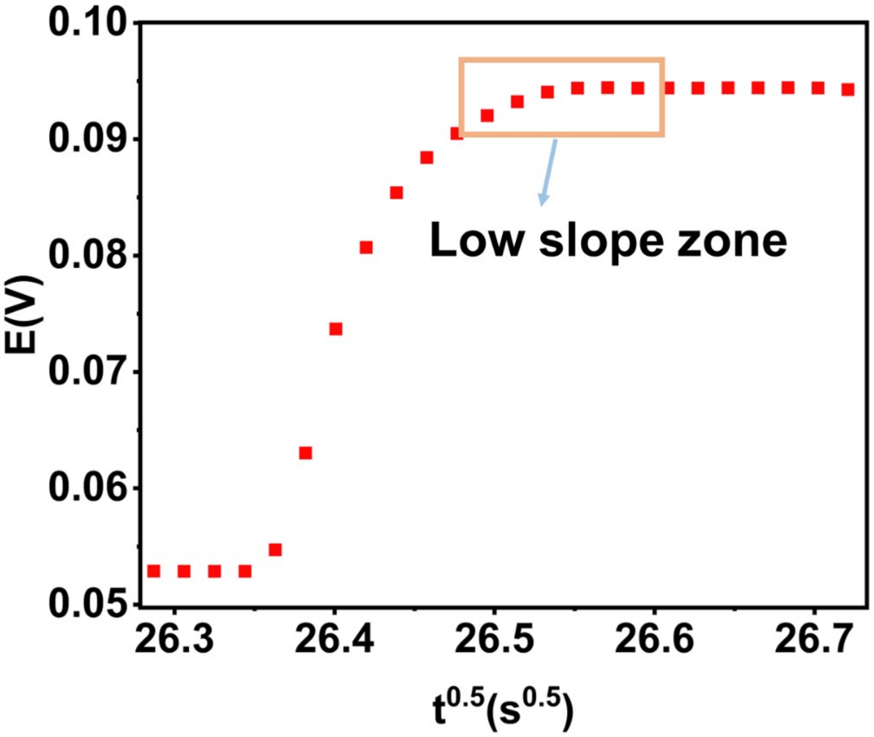

Figure S7. The select of low slope zone in E vs. $\sqrt{t}$ curve, from the framed area, the value of $\frac{dE}{d\sqrt{t}}$ can be determined by FDE method.

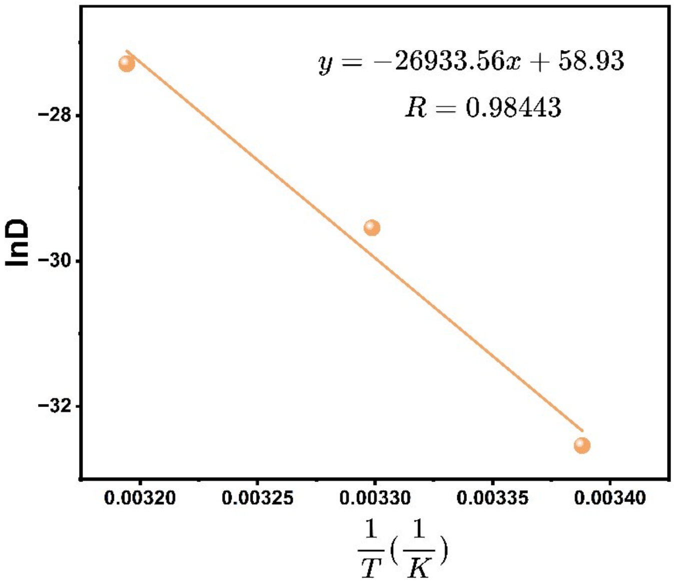

Figure S8: The fitted curve manufactured from x equals 0.2. In figure S8, the activation energy can be calculated from the equation of fitted curve equation and E_a=223.92KJ/mol