Electrochemical-assisted triple oxidation strategy to efficiently extract lithium from spent $LiFePO_4$

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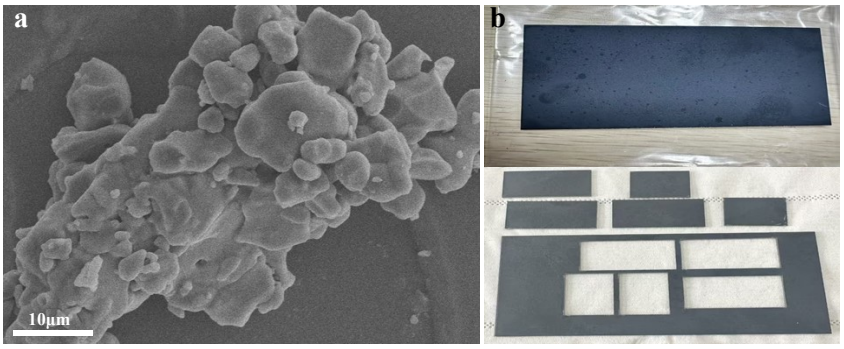

Fig. S1 (a) SEM image of as-fabricated Ti_4O_7 powder. (b) Photo of as -fabricated Ti_4O_7 electrode.

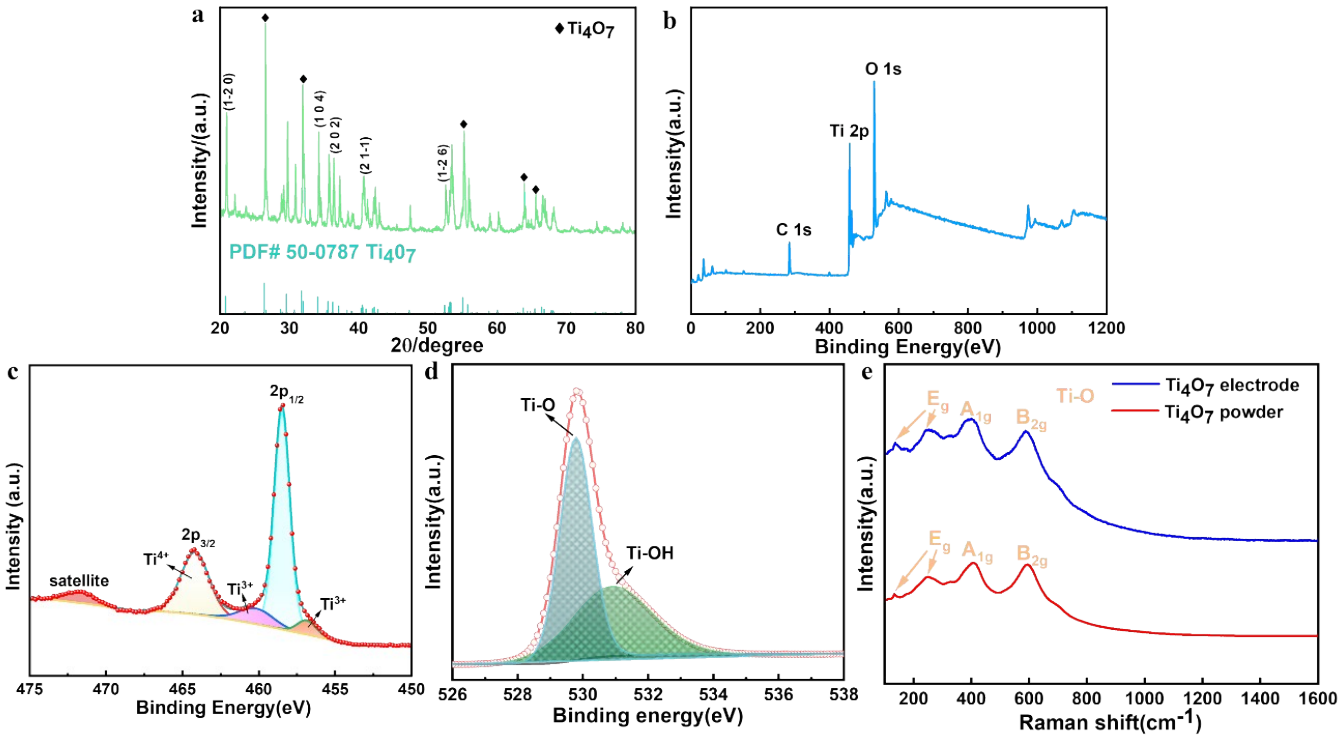

Fig. S2 (a) XRD patterns. (b) High resolution XPS survey, (c) Ti 2p, and (d) O 1 s spectrum of Ti_4O_7 electrode. (e) Raman spectra of Ti_4O_7 powder and electrode.

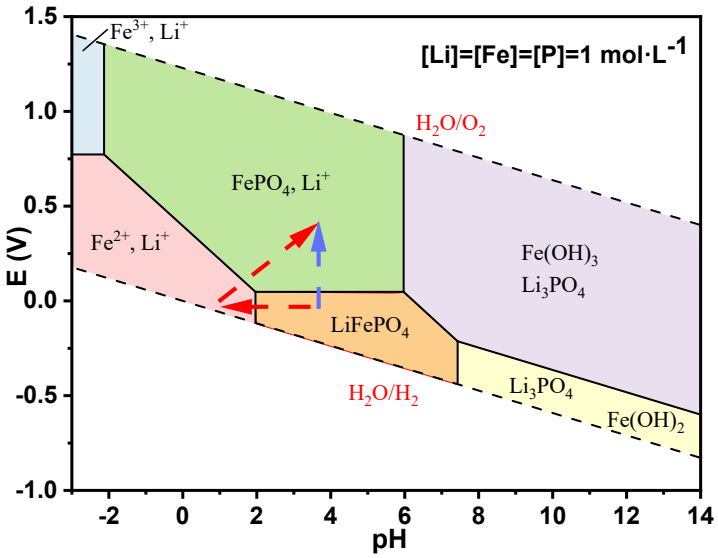

Fig. S3 Eh-pH phase diagram of Li-Fe-P-H_2O system.

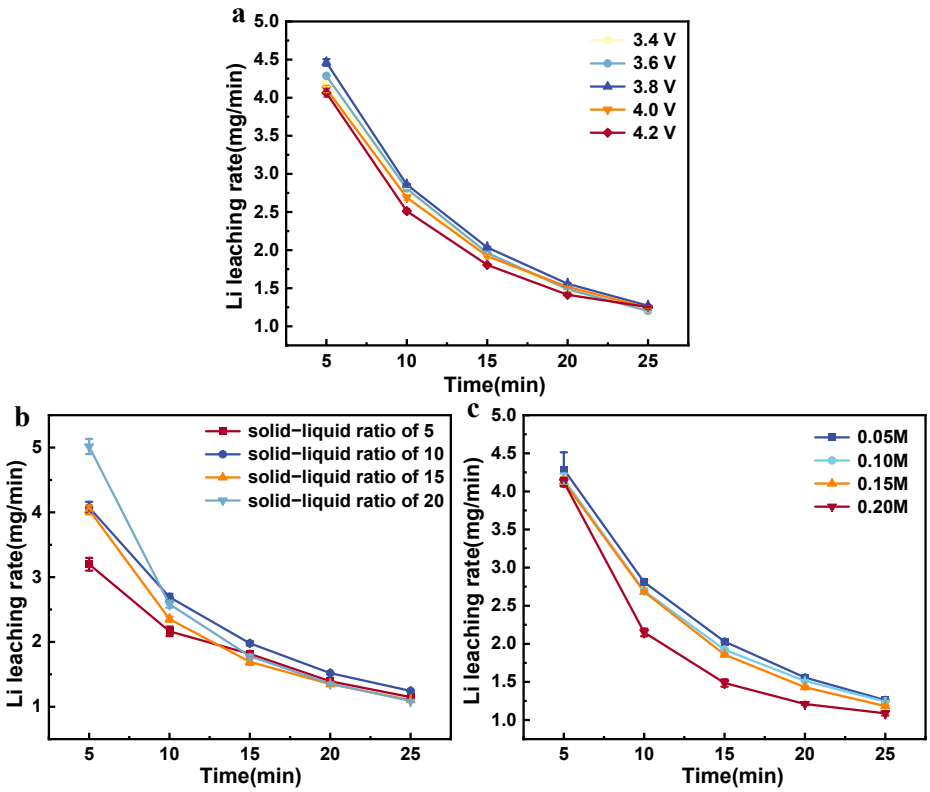

Fig. S4 (a) Comparison of lithium leaching via electrochemical-assisted leaching under different voltages, (b) Different solid-liquid ratios and (c) different electrolyte concentrations.

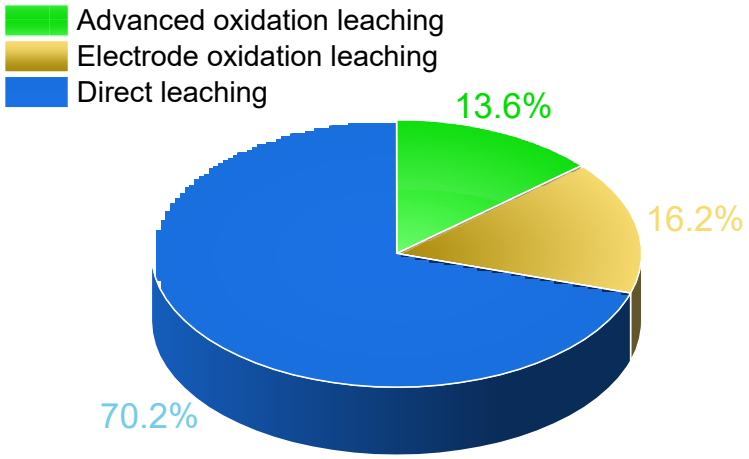

Fig. S5 Proportion of each part in the electrochemical assisted leaching system.

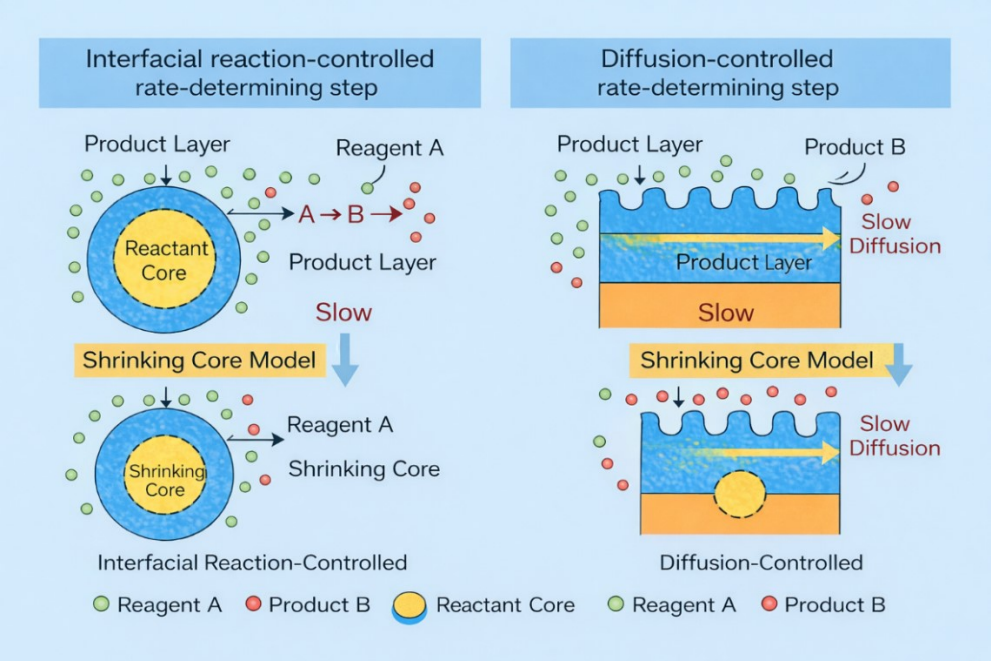

Fig. S6 Schematic diagram of shrinking core model.

The fundamental premise of this model is that solid particles are leached progressively from the outer surface towards the interior. As a result, the unreacted core diminishes continuously with the product layer growing gradually. Based on the distinct controlling steps, two typical kinetic equations can be deduced from the SCM.[64]

When the interfacial chemical reaction is the rate-controlling step, the relationship between the conversion rate "x" and time "t" can be expressed as **Eq. S1**:

$$1-(1-x)^{\frac{1}{3}}=kt \quad \textbf{(1)}$$

Among them, "k" denotes the apparent rate constant. This equation reveals that the conversion "x" increases in an approximately linear manner with time "t", reflecting the decisive influence of interfacial reaction rate on the overall leaching process.

In the case where the diffusion within product layer constitutes the rate-determining step, the kinetic equation is given by **Eq. S2**:

$$1-\frac{2}{3}x-(1-x)^{\frac{2}{3}}=kt \quad \textbf{(2)}$$

This expression indicates that the conversion rate gradually slows down as time increases, which is in line with the characteristics of a diffusion-controlled process. This expression indicates that the conversion "x" gradually slows down as time "t" increases, which is in line with the characteristics of a diffusion-controlled process. However, when neither of the two models is applicable, a third model, the hybrid control model is introduced. The kinetic equation is given by **Eq. S3**:

$$\frac{1}{3} * \ln(1-x) - 1 + (1-x)^{\frac{1}{3}} = kt \qquad \textbf{(3)}$$

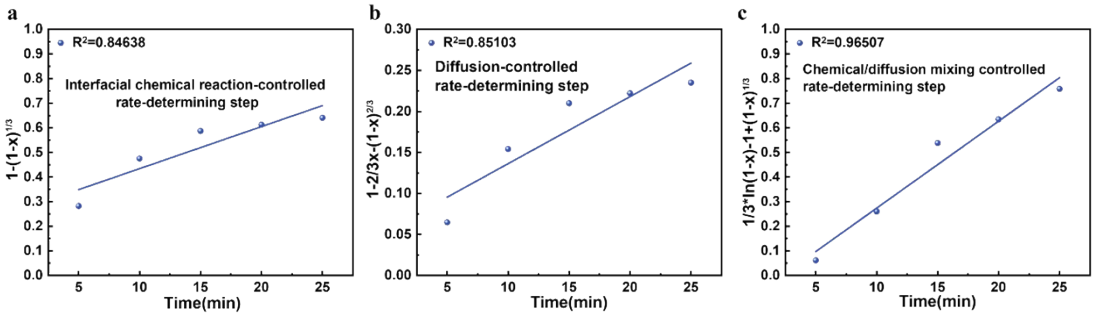

Fig. S7 (a) Chemical reaction rate control model fitting, (b) Diffusion control model fitting and (c) Chemical/ diffusion mixing controlled fitting by core shrinkage model.

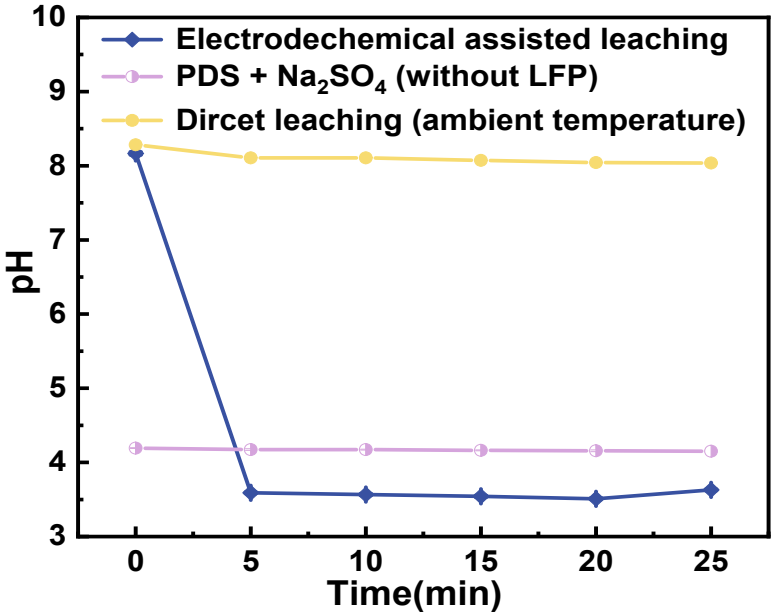

Fig. S8 pH images under different conditions.

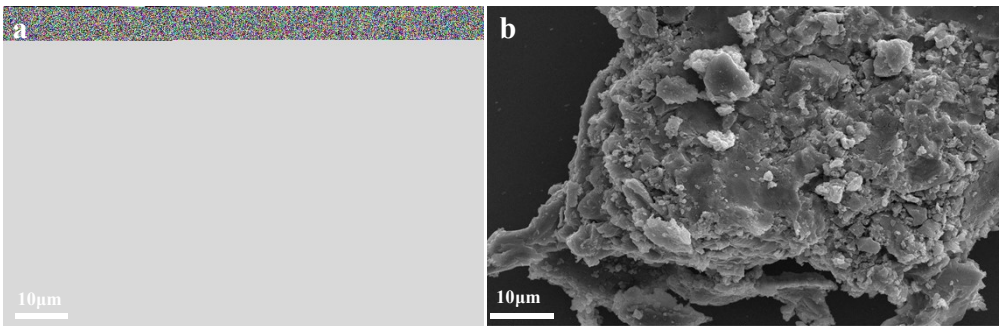

Fig. S9 (a) The Ti_4O_7 electrode before (a) and after (b) the reaction

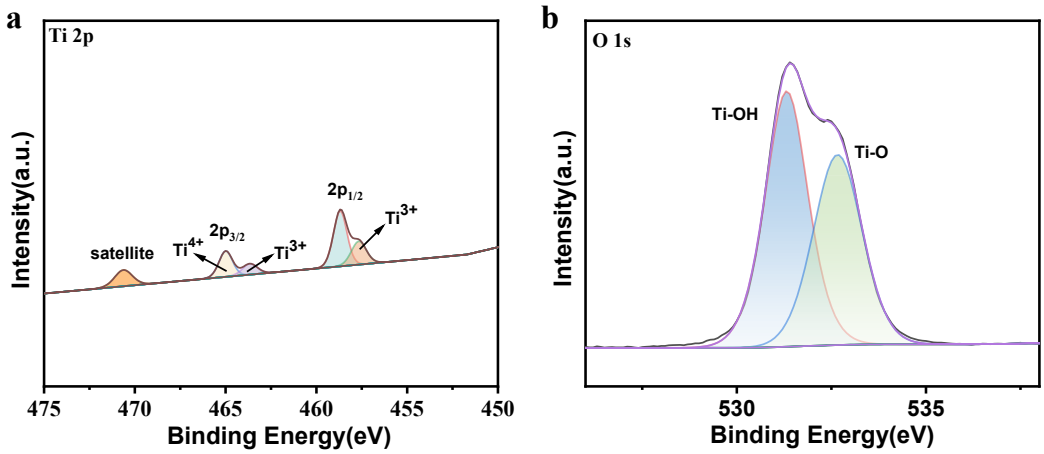

Fig. S10 High resolution XPS survey, (c) Ti 2p, and (d) O 1 s spectrum of Ti_4O_7 electrode after the reaction

Table. S1 ICP analysis (Ti dissolution) of the electrolyte under ten-cycle experiments

ELEM	Avg	Units
Ti	0.000366	ppm
Ti	0.000120	ppm
Ti	0.000800	ppm
Ti	0.000320	ppm
Ti	0.000238	ppm
Ti	0.000170	ppm
Ti	0.000183	ppm
Ti	0.000170	ppm
Ti	0.000220	ppm
Ti	0.000112	ppm