

Supplementary Information

Efficient regenerating of retired LiFePO_4 cathode by combining spontaneous and electrically driven processes

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Text S1:

The structure of equivalent circuit model

The internal resistance of the electrolytic cell can be equivalent to the following model:

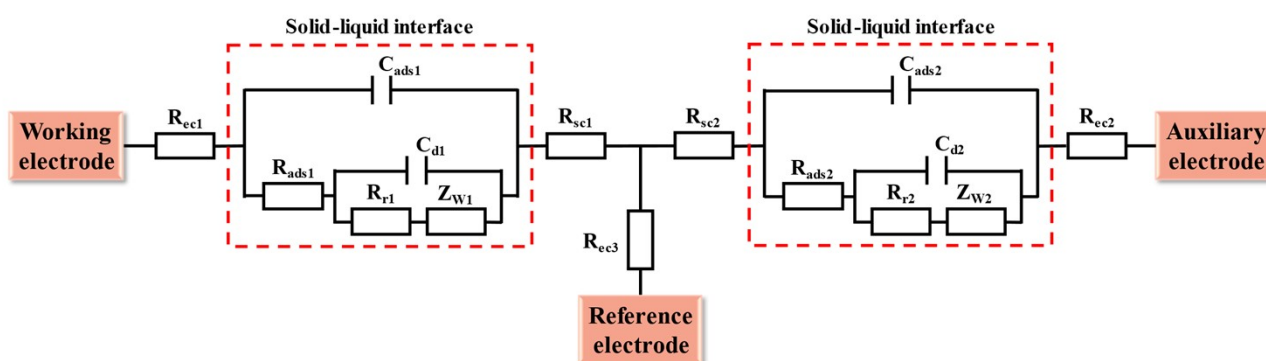


Fig. S1 The schematic diagram of equivalent circuit model

R_{ec1} , R_{ec2} and R_{ec3} : the electron conduction resistance in solid materials including working electrode, auxiliary electrode and reference electrode;

R_{sc1} and R_{sc2} : the electron conduction resistance in liquid solution;

R_{ads1} and C_{ads1} : the adsorption resistance and capacitance of working electrode surface;

R_{ads2} and C_{ads2} : the adsorption resistance and capacitance of auxiliary electrode surface;

C_{d1} and C_{d2} : the electrical double-layer capacitance between the solution and working electrode, auxiliary electrode;

R_{r1} and R_{r2} : the resistance of electrochemical reaction occurred on the working electrode surface and auxiliary electrode surface;

Z_{w1} and Z_{w2} : the concentration polarization resistance constituted of diffusion resistance and capacitance in working electrode surface and auxiliary electrode surface.

In addition, owing to the extremely small exposed area in liquid, the solid-liquid interface resistance between reference electrode and solution can be ignored reasonably.

In this work, the obsolete triphylite $\text{Li}_{1-x}\text{FePO}_4$ fixed by a platinum electrode clamp is applied to the working electrode, and the auxiliary electrode and reference electrode are the platinum-mesh electrode of 2×2 cm and Ag/AgCl reference electrode with saturated KCl solution, respectively. In general, Ag/AgCl reference electrode and the working electrode constitute a test circuit, and the system must be equal to a circuit breaker, owing to the potential of the working electrode is measured under equilibrium conditions and a infinitesimally small current. The working electrode and opposite electrode constitute another circuit, which is the circuit of the electrolytic cell to meet the balance of the electrochemical reaction. Therefore, in the structure of equivalent circuit model, the circuit with reference electrode can be ignored because of the current breaker, and the circuit between working electrode and auxiliary electrode provides an electron channel for the electrode reaction occurred in working electrode. Furthermore, the auxiliary electrode are usually required not to affect the reaction at the working electrode, thus equipped with large reactive surface and low resistance to eliminate the influence of excess resistance and capacitance.

According to the above analysis, the structure of equivalent circuit model can be simplified as the following model:

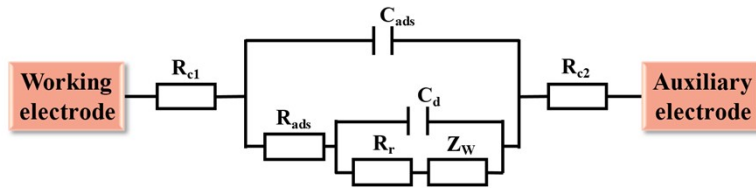


Fig. S2 The schematic diagram of equivalent circuit model after simplifying

R_{c1} and R_{c2} : the non-solid-liquid interface resistance consisting of solid electron conduction resistance and liquid ionic conduction resistance;

R_{ads} and C_{ads} : the adsorption resistance and capacitance in the working electrode surface;

R_r : the electrochemical reaction resistance of $\text{Li}_{1-x}\text{FePO}_4$ to LiFePO_4 ;

C_d : the interfacial double layer capacitance

Z_W : the concentration polarization resistance constituted of diffusion resistance and capacitance.

Text S2:

The analysis of control steps of lithium embedding process

In this work, the electrochemical oxidation reaction is occurred on the surface of working electrode, accompanied by the directional movement of electrons in the external circuit and the directional migration of ions in the solution near the working electrode, which is a typical electrode electrochemical reaction process.

The traditional electrode electrochemical reaction process can be divided into a varies of continuously steps as following:

(1) **Pre-liquid phase transfer step:** the transfer of reactants from the inside of the solution (or the inside of the liquid electrode) to the electrode surface.

(2) **Pre-conversion step:** some transformation steps of reaction particles before electrochemical reaction on the electrode surface or in the liquid layer near the surface, such as adsorption on the electrode surface, removal of hydration shell or complex ion decomposition, etc. These changes are often made without the participation of electrons.

(3) **Electrochemical reaction step:** the reactant particles gain or lose electrons at the electrode/solution interface and the electrochemical reaction is called the electron transfer step.

(4) **Post-conversion step:** the transformation steps of the product after electrochemical reaction on the electrode surface or in the liquid layer near the surface, including surface desorption, recombination, decomposition disproportionation and other chemical changes.

(5) **Post-liquid phase transfer step:** *a*: new phase is formed, such as the formation of gas, solid deposits, metal electro-crystallization. *b*: the reaction product is a soluble substance, which is transferred from the surface of the electrode to the interior of the solution or liquid electrode.

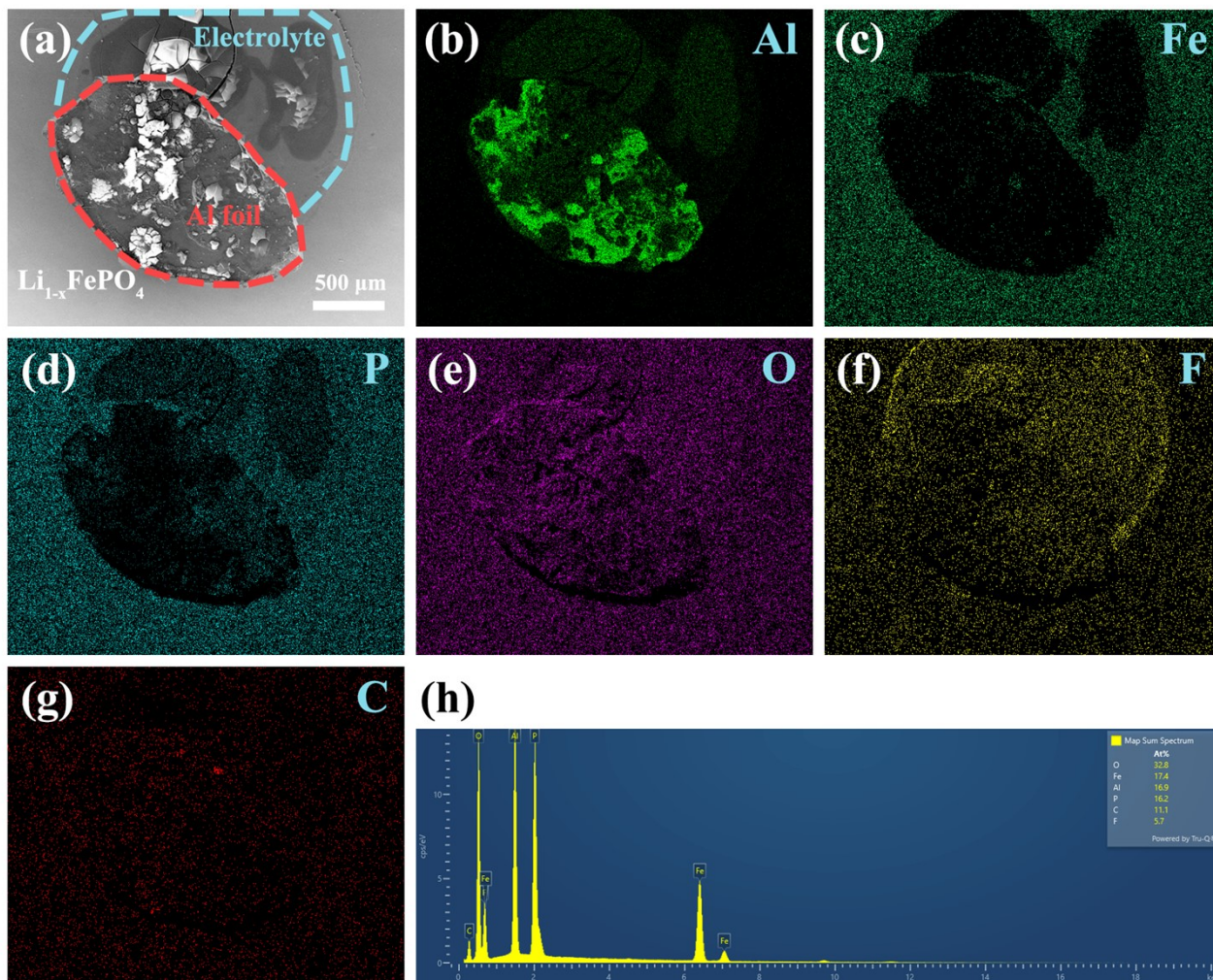


Fig. S3 (a) The SEM image of LiFePO_4 electrode sheet surface with locally active material shedding, (b) Al, (c) Fe, (d) P, (e) O, (f) F, (g) C, (h) EDX spectrum.

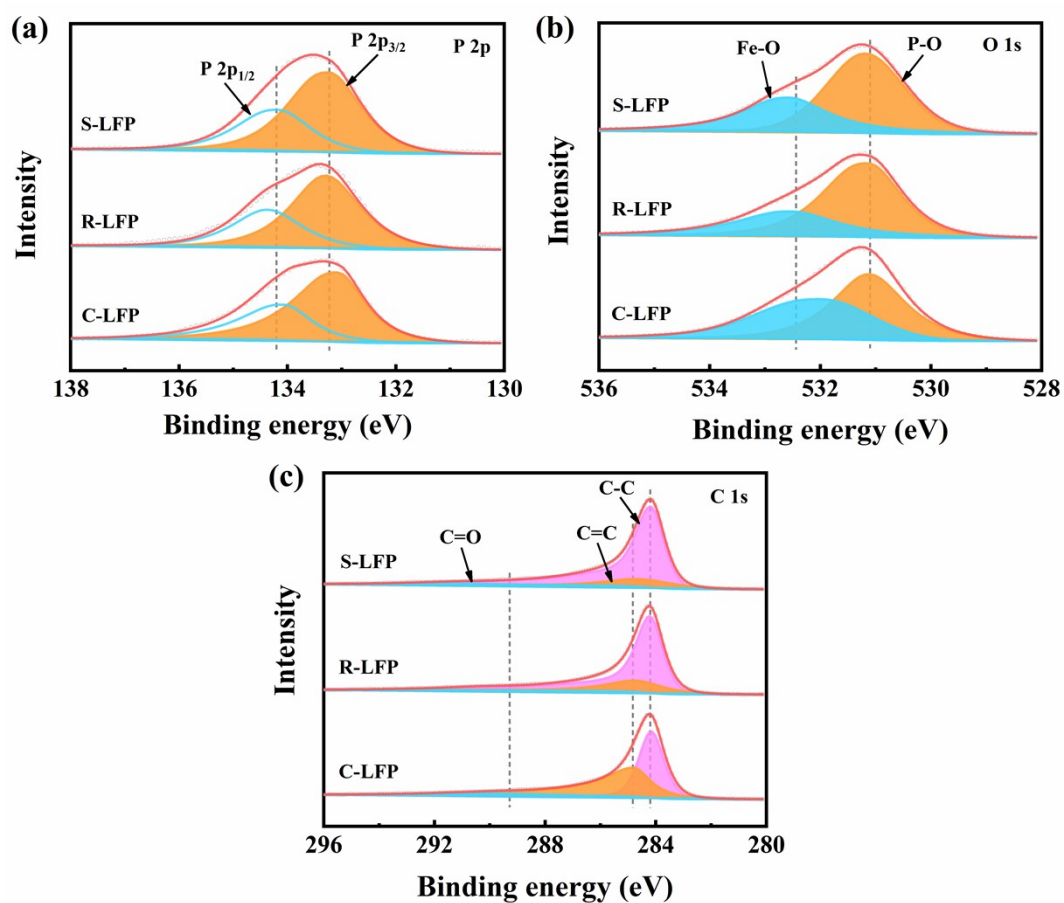


Fig. S4 The XPS spectra of S-LFP, R-LFP and C-LFP: (a) P 2p, (b) C 1s, (c) O1s.

Table S1 Rietveld refinement results of the S-LFP, R-LFP and C-LFP.

Samples	a(Å)	b(Å)	c(Å)	Volume(Å ³)
S-LFP	10.319205	6.001488	4.697390	290.912
R-LFP	10.320982	6.003517	4.691454	290.693
C-LFP	10.323543	6.004138	4.691373	290.790

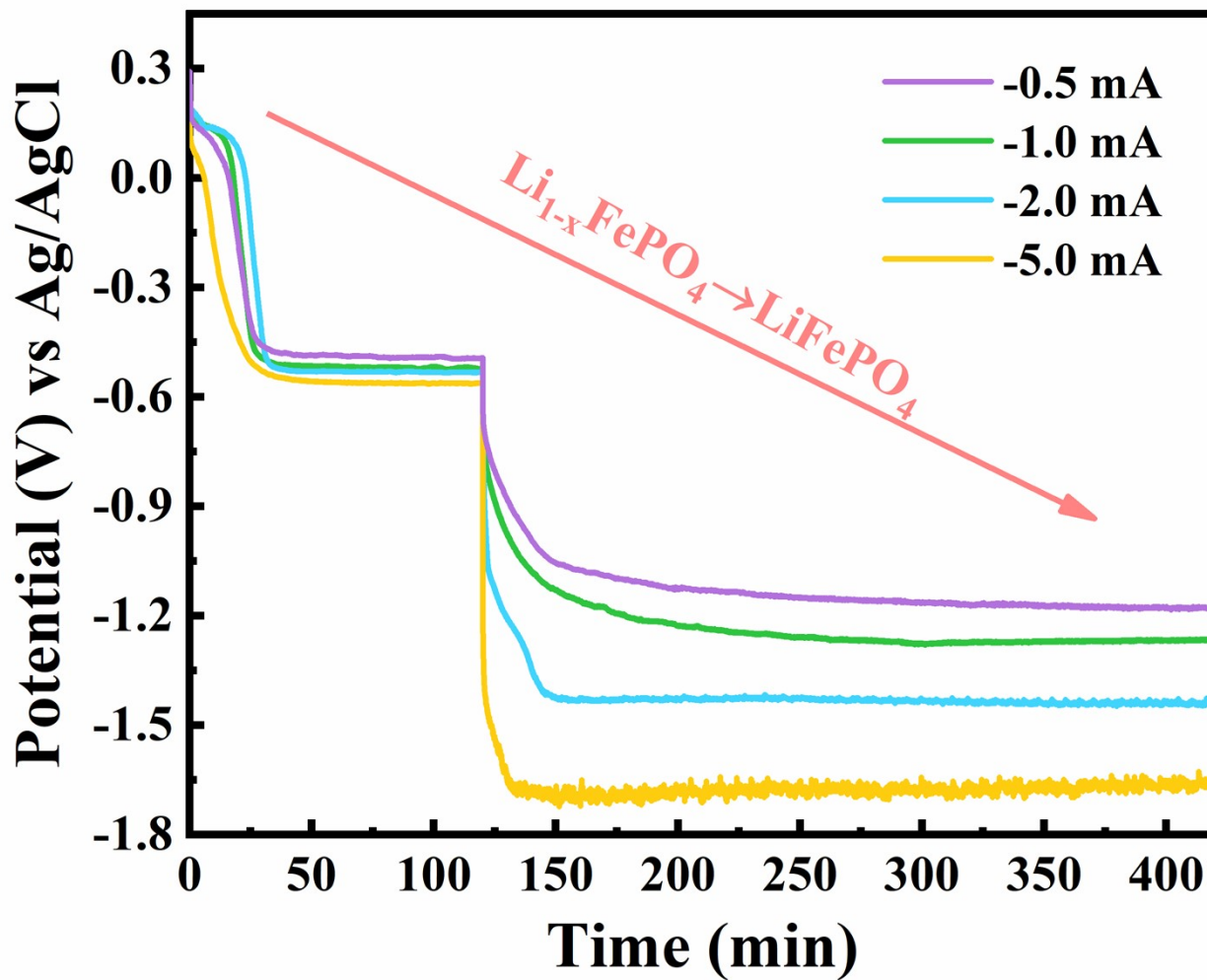


Fig. S5 The V-t curve at different impressed current.

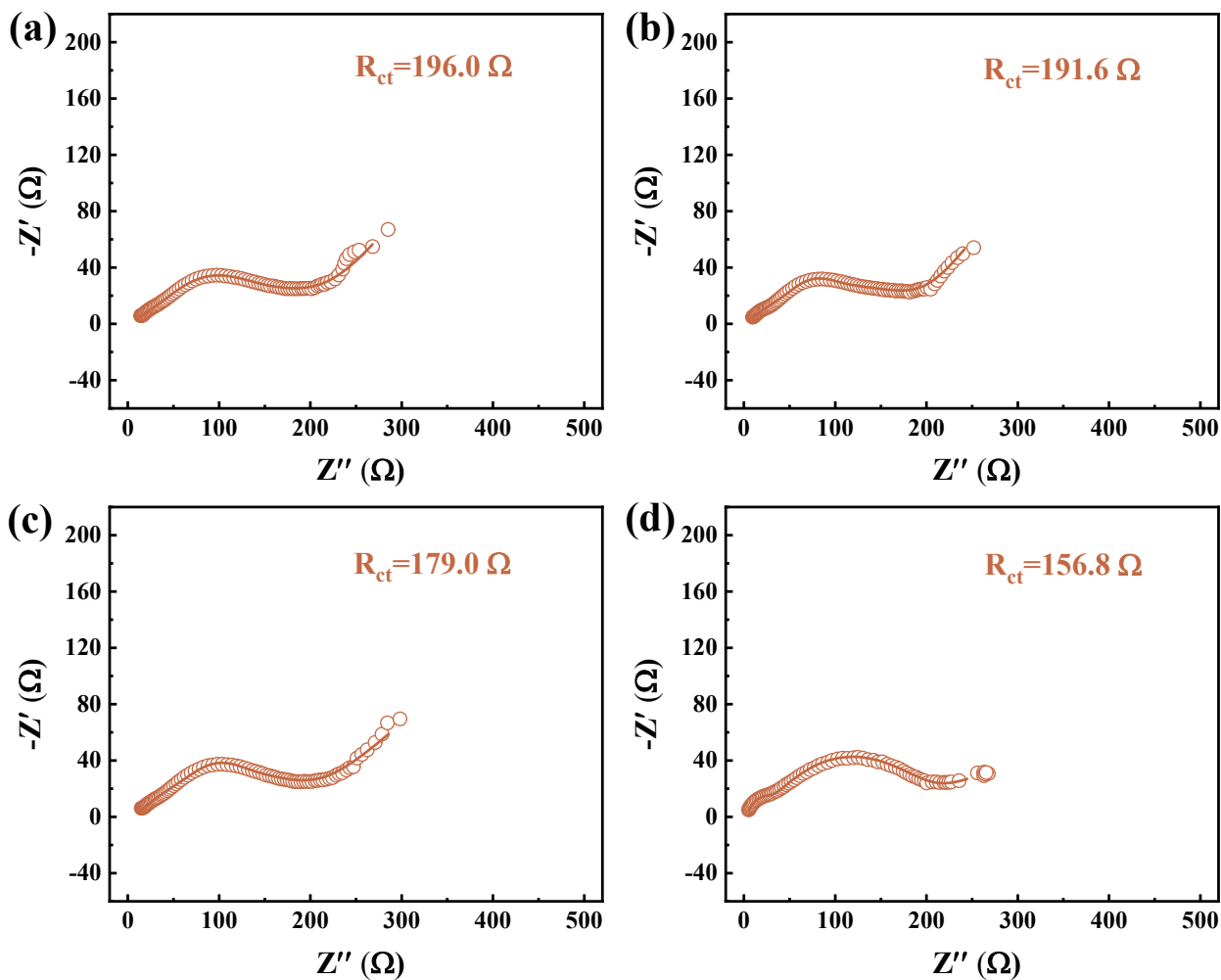


Fig. S6 The measured results of charge transition resistance at different Li_2SO_4 concentration before resting for two hours: (a) $0.1 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$; (b) $0.2 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$; (c) $0.5 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$; (d) $1.0 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$.

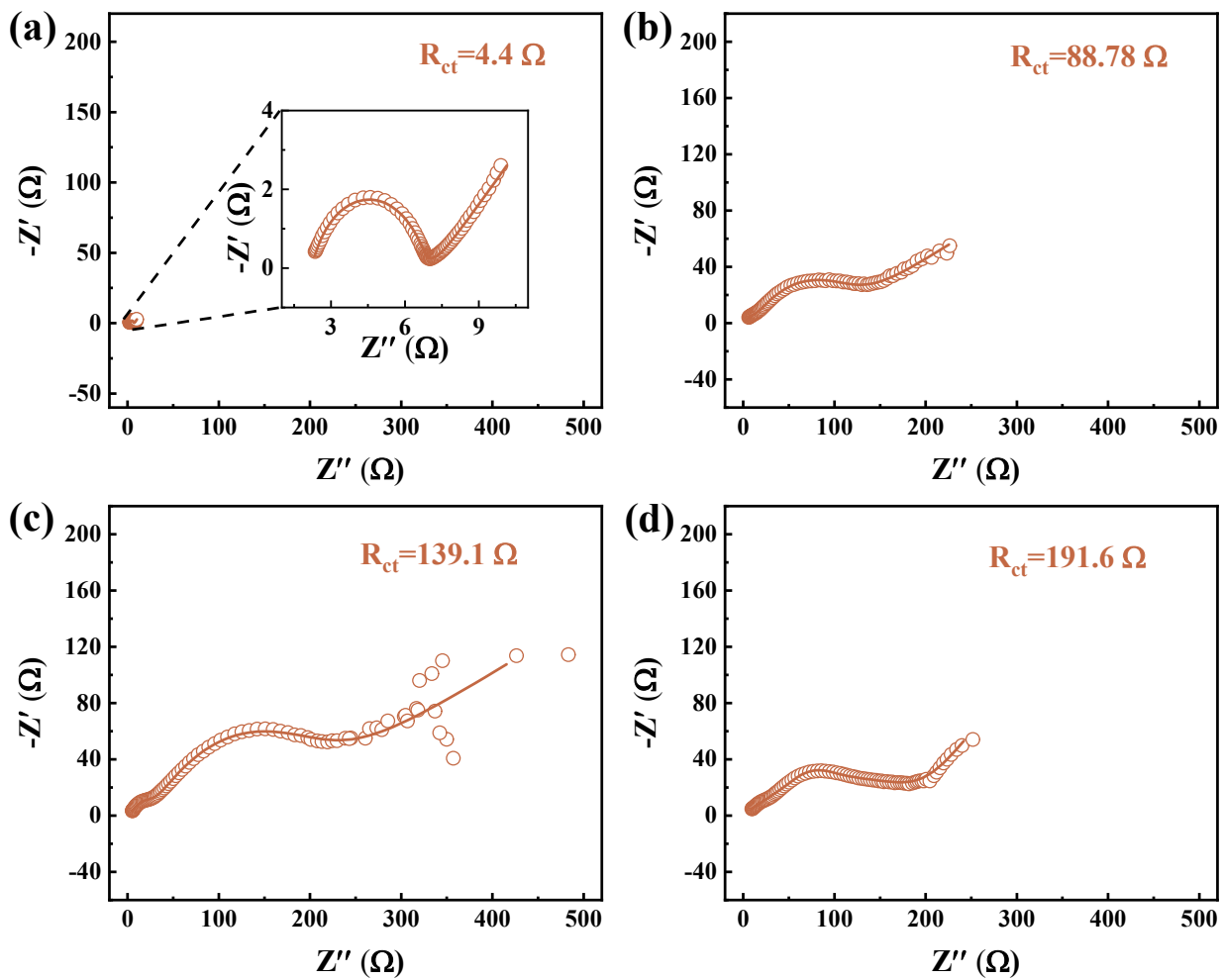


Fig. S7 The measured results of charge transition resistance at four samples with different lithium deficiency before resting for two hours: (a) $\text{Li}_{1.00}\text{FePO}_4$; (b) $\text{Li}_{0.65}\text{FePO}_4$; (c) $\text{Li}_{0.67}\text{FePO}_4$; (d) $\text{Li}_{0.69}\text{FePO}_4$.

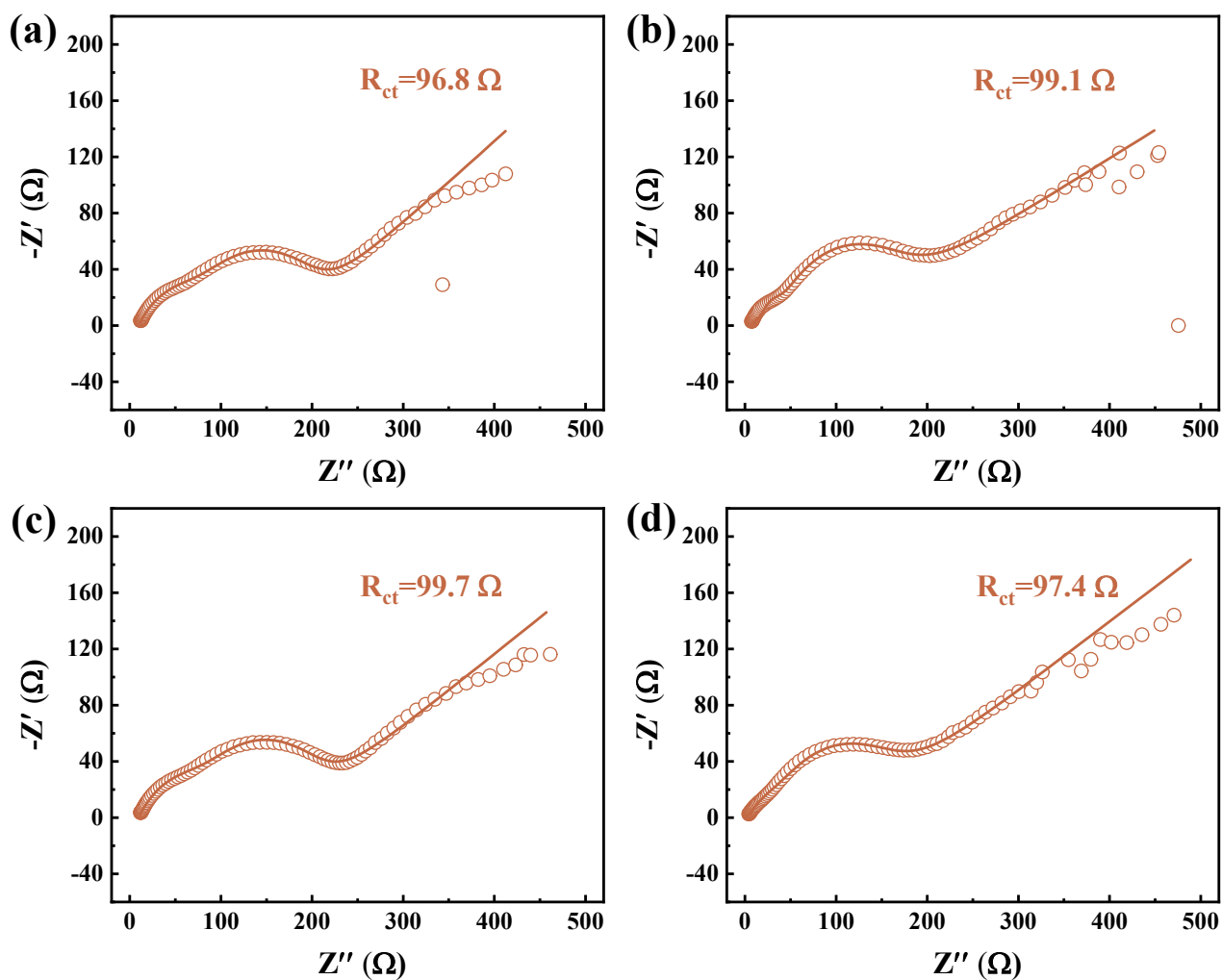


Fig. S8 The measured results of charge transition resistance at different Li_2SO_4 concentration after resting for two hours: (a) $0.1 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$; (b) $0.2 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$; (c) $0.5 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$; (d) $1.0 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$.

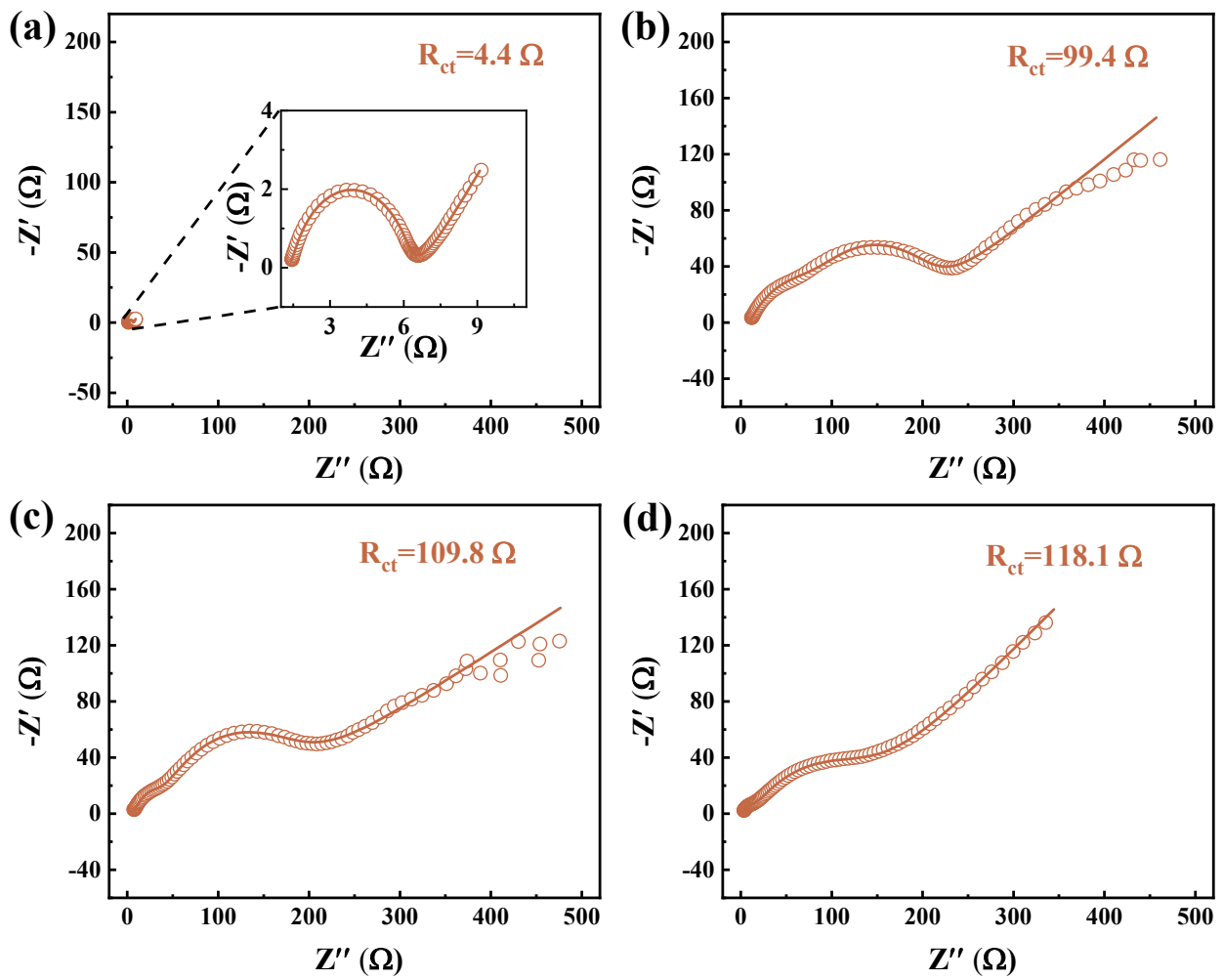


Fig. S9 The measured results of charge transition resistance at four samples with different lithium deficiency after resting for two hours: (a) $\text{Li}_{1.00}\text{FePO}_4$; (b) $\text{Li}_{0.87}\text{FePO}_4$; (c) $\text{Li}_{0.91}\text{FePO}_4$; (d) $\text{Li}_{0.94}\text{FePO}_4$.

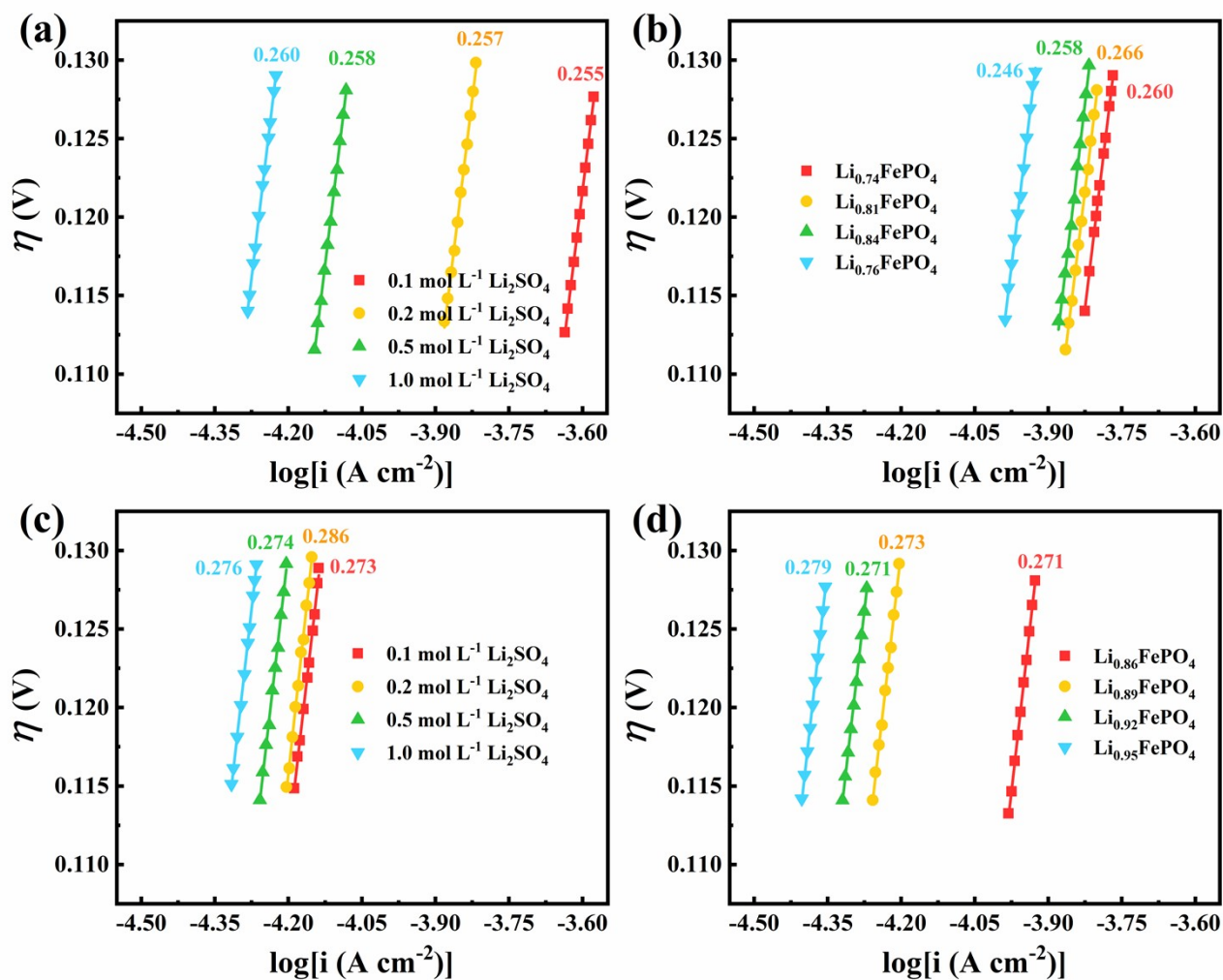


Fig. S10 The fitting results of Tafel slope under different Li_2SO_4 concentration and lithium deficiency: (a) different Li_2SO_4 concentration before resting for two hours, (b) different lithium deficiency before resting for two hours, (c) different Li_2SO_4 concentration after resting for two hours, (d) different lithium deficiency after resting for two hours.

Table S2 The error value of Tafel slope and intercept at different Li₂SO₄ concentration before resting for two hours.

Concentration	0.1 mol/L Li ₂ SO ₄	0.2 mol/L Li ₂ SO ₄	0.5 mol/L Li ₂ SO ₄	1.0 mol/L Li ₂ SO ₄
Slope	0.255±0.002	0.257±0.004	0.258±0.003	0.261±0.004
Intercept	1.040±0.007	1.110±0.014	1.180±0.010	1.230±0.004
<i>i</i> ₀ (10 ⁻⁵ A cm ⁻²)	8.394±1.146	4.797±2.039	2.670±1.043	1.960±0.393

Table S3 The error value of Tafel slope and intercept at four samples with different lithium deficiency before resting for two hours.

Sample	Li _{0.72} FePO ₄	Li _{0.81} FePO ₄	Li _{0.76} FePO ₄	Li _{0.84} FePO ₄
Slope	0.260±0.002	0.258±0.003	0.267±0.005	0.258±0.005
Intercept	1.106±0.006	1.108±0.010	1.147±0.020	1.145±0.019
<i>i</i> ₀ (10 ⁻⁵ A cm ⁻²)	5.601±0.718	5.138±1.043	5.254±1.845	3.796±1.368

Table S4 The error value of Tafel slope and intercept at different Li₂SO₄ concentration after resting for two hours.

Concentration	0.1 mol/L Li ₂ SO ₄	0.2 mol/L Li ₂ SO ₄	0.5 mol/L Li ₂ SO ₄	1.0 mol/L Li ₂ SO ₄
Slope	0.273±0.005	0.286±0.005	0.274±0.005	0.276±0.003
Intercept	1.257±0.023	1.319±0.021	1.282±0.021	1.307±0.011
<i>i</i> ₀ (10 ⁻⁵ A cm ⁻²)	2.601±0.988	2.537±0.884	2.183±0.798	1.863±0.389

Table S5 The error value of Tafel slope and intercept at four samples with different lithium deficiency before resting for two hours.

Sample	Li _{0.84} FePO ₄	Li _{0.89} FePO ₄	Li _{0.92} FePO ₄	Li _{0.94} FePO ₄
Slope	0.276±0.002	0.274±0.005	0.273±0.002	0.281±0.003
Intercept	1.214±0.009	1.282±0.021	1.292±0.009	1.353±0.011
<i>i</i> ₀ (10 ⁻⁵ A cm ⁻²)	4.021±0.595	2.183±0.798	1.865±0.289	1.551±0.321

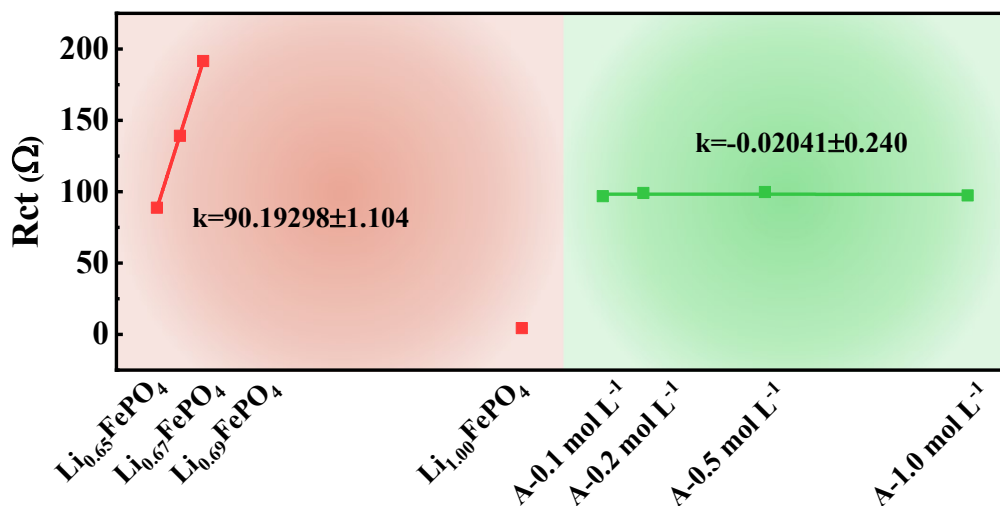


Fig. S11 The fitting results and slopes of electrochemical reaction resistance for different lithium deficiency before resting for two hours and different Li_2SO_4 concentration after resting for two hours.

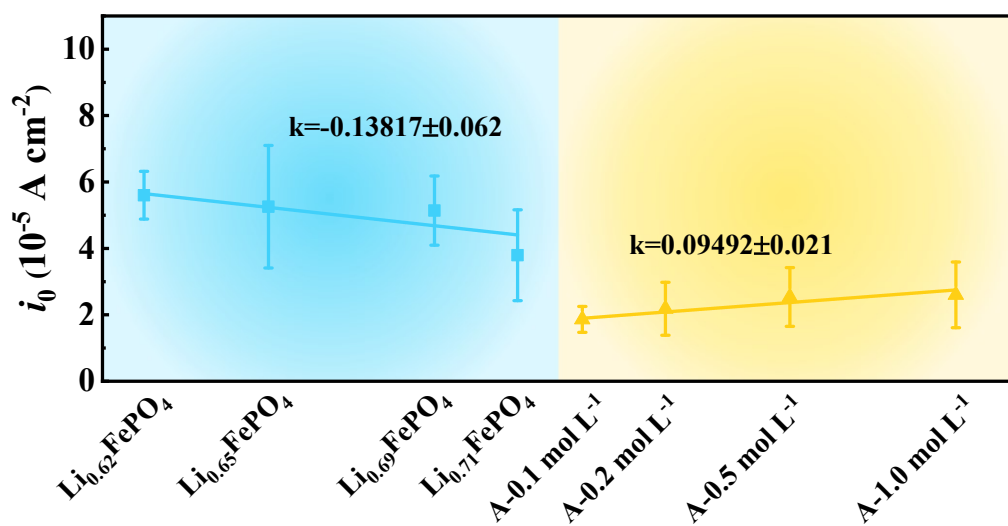


Fig. S12 The fitting results and slopes of exchange current density for different lithium deficiency before resting for two hours and different Li_2SO_4 concentration after resting for two hours.