Supplementary information

Reaction-passivation-driven delamination of spent LiFePO₄ cathodes and their upgrading to high-efficient catalysts for hydrogen evolution

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Experimental Section

Materials

2-hydroxyphosphonic acid (HPAA), amino tri(methylene phosphonic acid) (ATMPA), polyhydric alcohol phosphate ester (PAPE), and bis-1,6-hexamethylenetriamine penta(methylene phosphonic acid) (BHMTPMPA), HCl, H₃PO₄, and ammonia water were purchased from Aladdin Ltd., and the spent batteries were provided by Anhui Eagoal New Energy Group Co., Ltd. All reagents were employed as received. Deionized water with a resistivity of 18.25 M Ω ·cm was used in all experiments.

HPAA-assisted delamination of LiFePO₄ cathode sheets

2 g of LiFePO₄ cathode sheets were cut into 2×2 cm² pieces and placed in 30 mL HPAA aqueous solution of different concentration at 25°C. The separation process was carried out under continuous stirring (400 rpm) to achieve effective separation. The pH of the solution was adjusted with HCl or ammonia aqueous solution, and the separation performance of other organic acids was evaluated using the same procedure as for HPAA.

Synthesis of FexP catalysts for hydrogen evolution

50 mg of FePO₄ slag and 10 mg of graphene were mixed thoroughly in a mortar. Subsequently, the resulting mixture was transferred to a tube furnace and heated to 650°C at a rate of 3°C min⁻¹ for 2 hours in a H₂-Ar mixed atmosphere (5 vol% H₂) with a flow rate of 20 sccm. Then cooled to room temperature at the same rate, yielding Fe_xP/G(10). The synthesis of Fe_xP/G(15) was identical to that of Fe_xP/G(10), with the only different amount of graphene.

Characterization

The XRD analysis was performed using a MiniFlex 600X-ray diffractometer. The sample's morphology and chemical composition were examined using a Scanning Electron Microscope (SEM) (SUPRATM 40). The surface element composition of the separated Al foil was analyzed using X-ray photoelectron spectroscopy (XPS, Kratos Axis supra+). Fourier Transform Infrared (FTIR) spectroscopy was performed with a Thermo FTIR spectrometer (Nicolet Summit Lite). The metal leaching rate was quantified by inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP PRO). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded using JEM-2100.

Electrochemical measurement

The electrochemical tests were performed utilizing a CHI760E workstation. A three-electrode system comprising an Ag/AgCl (saturated KCl) reference electrode, a graphite rod counter electrode, and the catalyst dripped onto a glassy carbon electrode (actual working area: 0.07 cm⁻²) as the working electrode, was employed for all electrochemical measurements. The electrolyte used was

 $0.5 \text{ M H}_2\text{SO}_4$ solution. To prepare the catalyst ink, 6 mg of the fresh catalyst was mixed with 20 µL Nafion solution (5 wt%), 600 µL of ethanol and 380 µL of deionized water. The resulting mixture was then sonicated for 60 minutes to obtain a homogenous suspension. 10 µL of the catalyst ink was drop-coated onto a 3 mm diameter glassy carbon electrode every test. The linear sweep voltammetry (LSV) measurements were conducted at a scan rate of 5 mV s⁻¹, and all potentials were subsequently converted to the reversible hydrogen electrode (RHE) reference scale using the formula:

$$E$$
 (vs. RHE) = E (vs. Ag/AgCl) + 0.197 + 0.0591*pH.

The Tafel slopes were determined from the LSV plots using the equation:

$$\eta = a + b \log|j|$$

where η , b, and j denote overpotential, Tafel slope, and current density, respectively. Electrochemical impedance spectroscopy (EIS) characterization was carried out over a frequency range of 1 Hz to 100 kHz. The durability of Fe_xP/G(10) was assessed through cyclic voltammetry (CV) with the scan range from 0 to -0.3 V vs. RHE.



Figure S1. Schematic diagram of FePO₄ upgrading to iron phosphide.



Figure S2 The XRD patten of FexP/G (10).



Figure S3 (a) TEM and (b) HRTEM images of $Fe_xP/G(10)$.



Figure S4 EDS element mapping of $Fe_xP/G(10)$.



Figure S5 The equivalent electrical circuit model used for EIS analysis.



Figure S6 The double-layer capacitance (C_{dl}) extracted from the slop of average current density (Δj =(ja-jc)/2) against the scan rate.



Figure S7 the chronoamperometry curve.

HER catalysts	E ₁₀ (mV)	Tafel slope(mV [.] dec ⁻¹)	Electrolyte	Ref.
FeP/G(10)	88	87	0.5 M H ₂ SO ₄	This work
FeP-GS	123	50	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	1
FeP@NC	135	78	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	2
FeP/3DG20	113.2	65.84	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	3
FeP	96	39	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	4
FeP/NCNSs	114	64	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	5
FeP@PPy	103.1	49.2	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	6
CoFeP/3D RGO	110	53	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$	7

Table S1. The comparison of the HER activity of the FeP/G(10) with the recently reported catalysts.

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