A Recrystallization Approach to Repairing Spent LiFePO$_4$ Black Mass

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Table S1 ICP-OES result of untreated/repaired (300°C treated) spent LFP.

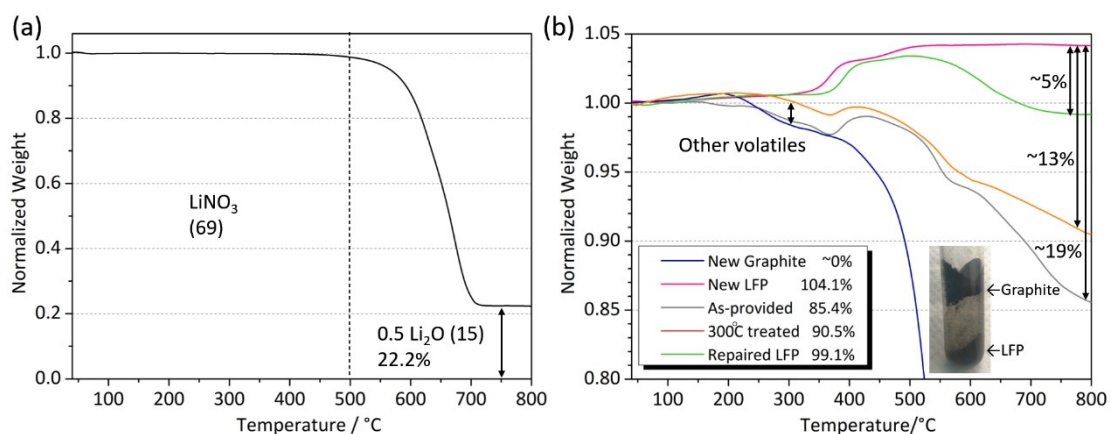| Sample	Untreated			Repaired		
	Li	Fe	P	Li	Fe	P
Weight ratio	~3.24%	28.71%	16.2%	~4.07%	32.65%	18.09%
Atomic ratio	0.904	1	1.019	1.003	1	0.999

Fig. S1 TG curves of (a) LiNO$_3$ pyrolysis and (b) different samples (the 300°C-treated sample was not processed by the centrifuging separation, the inserted image is a photograph of the 300°C-treated sample after separation).

Calculation of Gibbs Free Energy

The Gibbs free energy change of related reactions in Table 1 was calculated based on the following formula (with data & reference in Table S2):

$$\Delta_r G_T^{\ominus} = \Delta_r H_T^{\ominus} - T\Delta_r S_T^{\ominus} \tag{S1}$$

$$\Delta C_{P,m}(T) = \Delta a + \Delta bT + \Delta cT^{-2} \tag{S2}$$

$$\Delta_r H_T^{\ominus}$$
$$= \Delta_r H_{298}^{\ominus} + \int_{298.15}^{T} \frac{\Delta C_P dt}{T} dt = \Delta_r H_{298}^{\ominus} + \Delta a(T - 298.15) + \frac{\Delta b(T^2 - 298.1}{2} \tag{S4}$$
$$298.15^{-2})$$

$$\Delta_r S_T^{\ominus}$$
$$= \Delta_r S_{298}^{\ominus} + \int_{298.15}^{T} \frac{\Delta C_P dt}{T} dt = \Delta_r S_{298}^{\ominus} + \Delta a ln(T - 298.15) + \Delta b(T$$

Table S2 Thermodynamic properties of related substances.

Substance	$\Delta_f H_{298}^{\ominus}$ (kJ/mol)	$S_{298}^{\ominus}$ (J/mol·K)	$\Delta C_{P,m}(T) = a + bT + cT^{-2}$ (J/mol·K)			Ref.
			a	10^3 b	10^{-5} c	
*$FePO_4$	-1297.000	100.000	122.490	55.100	-40.380	1
$FePO_4$	-1289.56	108.51				2
$FePO_4$	-1220.4					3
*$LiFePO_4$	-1591.023	130.950	102.680	95.700	-14.00	4, 5
$LiFePO_4$	-1514.8	136.75				2
$LiFePO_4$	-1392.45					3
$LiNO_3$	-483.1	90	78.73	191.74		6, 7
Li_2O	-598.73	37.91	66.92	17.27	-17.7	8
LiOH	-484.67	42.68	50.168	34.476	-9.498	8
Li_2CO_3	-1216.038	90.169	42.530	177.399		8
Li (BCC)	0	29.08	13.941	34.359		8
N_2 (g)	0	191.5	27.86	4.28		8
NO_2 (g)	33.1	239.9	35.68	22.91	-4.7	8
C	0	5.740	0.109	38.940	-1.481	8
O_2 (g)	0	205.04	29.96	4.18	-1.674	8
CO (g)	-110.541	197.660	28.409	4.100	-0.460	8
CO_2 (g)	-393.505	213.770	44.141	9.037	-8.535	8
Fe_2O_3	-824.248	87.404	98.282	77.822	-14.853	8
P_4O_{10}	-3009.936	228.781	149.754	324.762	-31.062	8
H_2O (l)	-241.826	188.959	29.999	10.711	0.335	8

Notably, LiFePO$_4$ and FePO$_4$ have multiple reported thermodynamic data with considerable variation, we chose the data (*) with completed a/b/c factors for better temperature-dependent calculation. In fact, the calculated $\Delta_r G_{298}^{\Theta}$ of LFP half-cell reaction (Li + FePO$_4$ = LiFePO$_4$) is -294.57 kJ/mol and its emf value (3.054V) is slightly deviated from the actual experimental result (3.425V). Therefore, the calculated data in Table.1 may contain a minor bias of ~32 kJ/mol, thus we adjusted the value based on the correct emf value and provided an emendatory table (Table.S3). Fundamentally, the variation does not affect the comparison of re-lithiation reactions with different Li salt, since they shared the same FePO$_4$ → LiFePO$_4$ procedure and the thermodynamic data of other common inorganics were well-established.

Table S3 Emendatory standard Gibbs free energy change for related reactions.

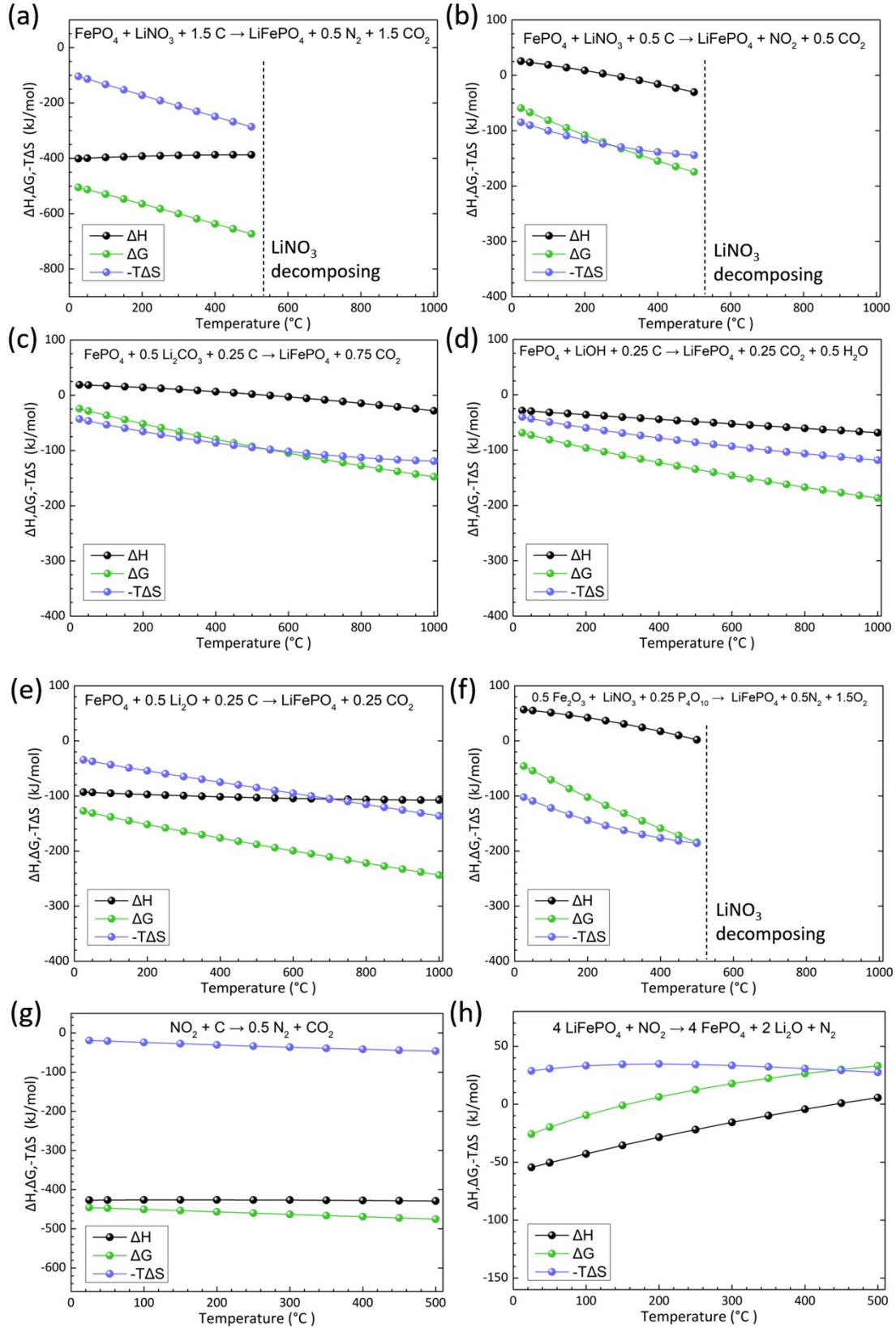| №	Reaction	$\Delta_r G_{298}^{\Theta}$ (kJ mol^{-1})
1	FePO$_4$ + Li → LiFePO$_4$	-326.58
2	FePO$_4$ + 0.5 Li$_2$CO$_3$ + 0.25 C → LiFePO$_4$ + 0.75 CO$_2$	-55.87
3	FePO$_4$ + LiOH + 0.25C → LiFePO$_4$ + 0.25 CO$_2$ + 0.5 H$_2$O	-100.79
4	FePO$_4$ + 0.5 Li$_2$O + 0.25C → LiFePO$_4$ + 0.25 CO$_2$	-159.38
5	FePO$_4$ + LiNO$_3$ + 0.5 C → LiFePO$_4$ + NO$_2$ + 0.5 CO$_2$	-91.45
6	FePO$_4$ + LiNO$_3$ + 1.5 C → LiFePO$_4$ + 0.5 N$_2$ + 1.5 CO$_2$	-537.06

Fig. S2 Temperature dependences of the calculated standard enthalpy change, the $-T\Delta S$ value and the standard Gibbs free energy change of the related reactions.
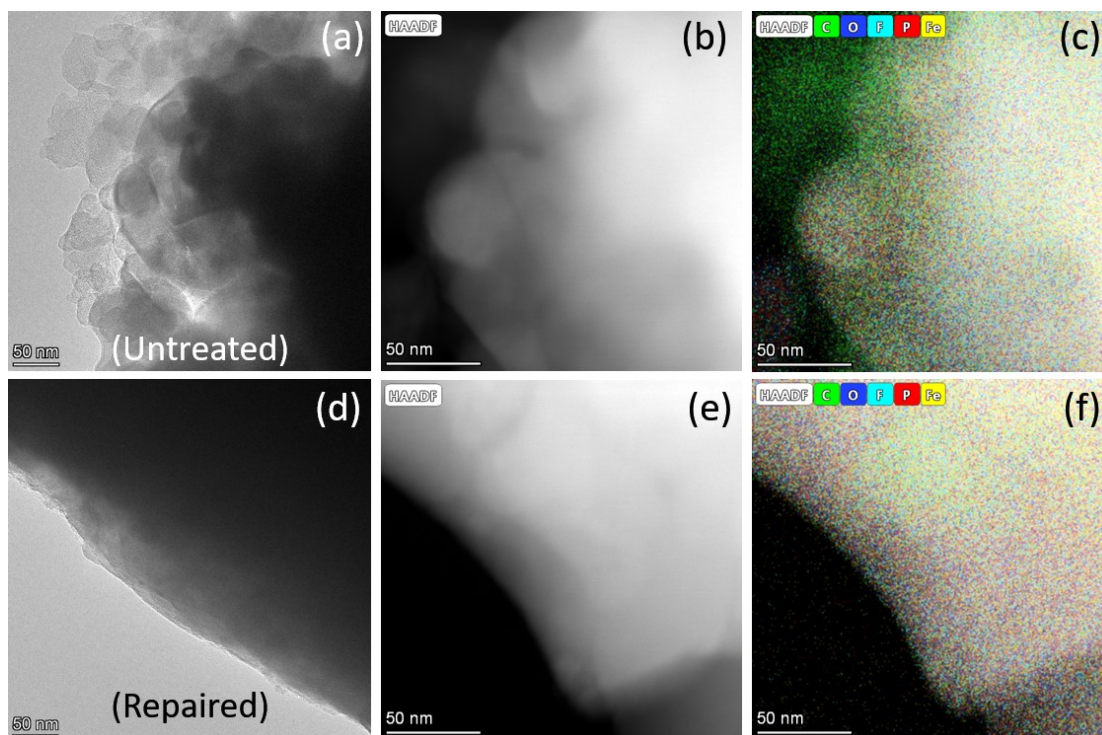
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Structural Characterization

Fig. S3 TEM images and corresponding STEM(HAADF)/EDS mapping of the (a)(b)(c) untreated and (d)(e)(f) repaired (300°C treated) spent LFP.
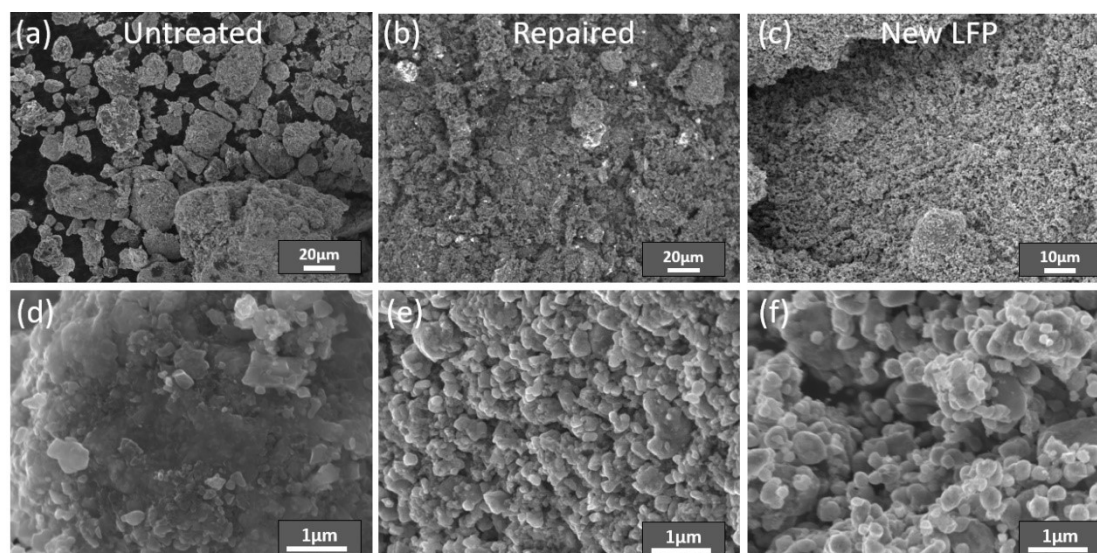

Fig. S4 SEM images of (a)(d) untreated, (b)(e) repaired spent LFP and (c)(f) new LFP.
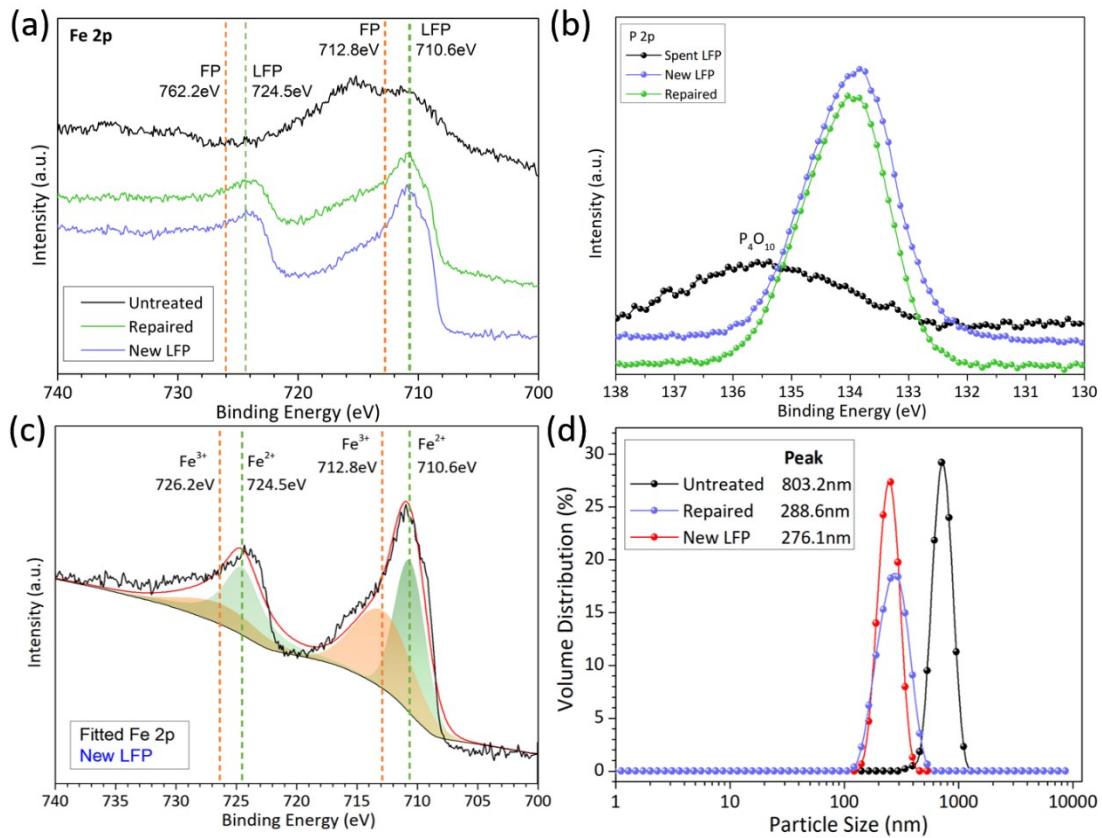
Fig. S5 XPS spectra of untreated/repaired spent LFP and new LFP: (a) Fe 2p; (b) P 2p and (c) fitted Fe 2p of new LFP; (d) Particle size distribution of untreated/repaired spent LFP and new LFP.
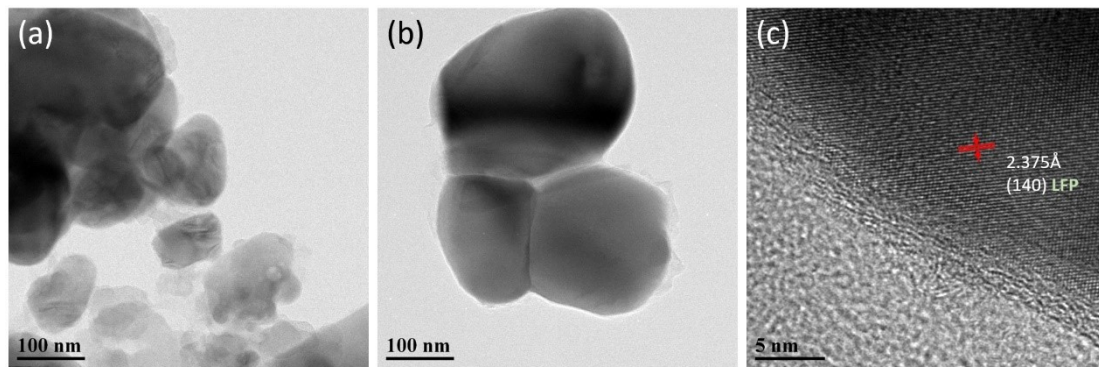

Fig. S6 TEM images of (a) the repaired spent LFP and (b)(c) commercial new LFP.

Practicability
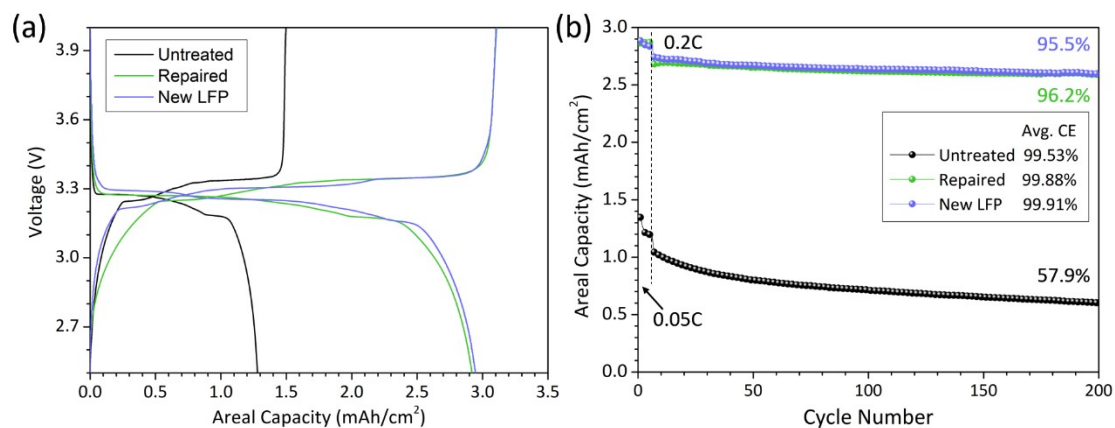
Fig. S7 (a) Full-cell initial charge/discharge curves (0.05C) and (b) cycling stability of untreated/repaired spent LFP and new LFP cathode film (~20mg/cm^2) paired with commercial graphite anode (the retention rates of each sample were calculated based on their discharge capacity at the 10th cycle).

Fig. S8 Optical microscopic images of cathode film prepared with (a) untreated spent LFP and (b-e) repaired mixture sample treated in different temperatures and (f) commercial new LFP (with their measured compaction density marked on the top).

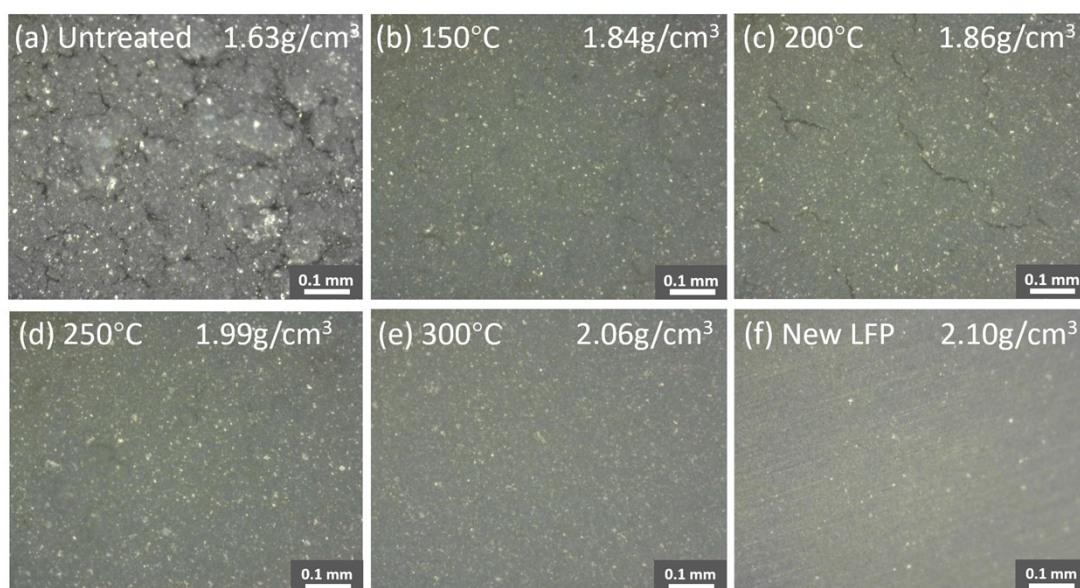The CO_2 and NO_2 emission of the heating process were investigated by mass spectrometry (MS). Typically, 0.08g sample mixture was sealed in a 20ml glass vessel with brass cap (filled with air) and heated to 300°C for 30min and naturally cooled down to room temperature. The gas sample within the vessel was obtained by sampling needle (0.5ml) and injected to the MS intake and tested with retention time of 2min. For comparison, the ambient air was tested in the same procedure. The CO_2 emission of the heated mixture can be semiquantitative estimated by the integral area of CO_2 peak (m/z=44) of the gas sample and air (as control sample). As result, the integral area of CO_2 peak in the sample is ~4.1 times higher than the CO_2 peak in ambient air (0.036%). Therefore, the estimated CO_2e of the 0.08g mixture is ~3.81mg (4.1*0.036*0.02L*1.29g/L), assuming the CO_2 was evenly dispensed in the 20ml vessel without surface adsorption. The spent LFP content in mixture is about 90% thus the direct CO_2e of repairing 1kg spent LFP with this method is ~0.053kg. Additionally, the NO_2 in the gas sample was barely detectable (less than 10% intensity of the CO_2) thus we do not further discuss the elimination of nitric oxides. The trace amount of NO_x released during the repair process can be simply neutralized by whitewash tail gas treatment, along with the PF_5 derived from residual electrolyte. Theoretically, the maximum direct CO_2e in this method is 0.076 kg/kg (assuming the 8wt% $LiNO_3$ was totally reduced by carbon, as the reaction **5**) and the maximum NO_2 emission is 0.053 kg/kg (assuming the $LiNO_3$ was all decomposed in to NO_2, corresponded to the reaction **4** in Table.1). The concentration of CO_2 and NO_2 are co-related in a sealed environment (reaction **15**) with the presence of abundant carbon on spent LFP. Therefore, the estimated NO_2 emission of the heating process is 0.023 kg/kg (0.08%) at most.
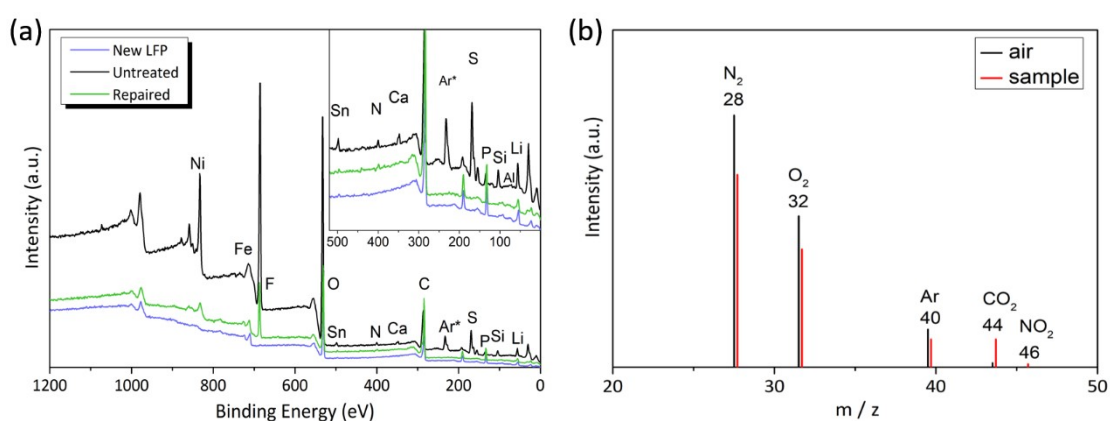

Fig. S9 (a) XPS survey scan of untreated/repaired spent LFP and purchased new LFP; (b) mass spectra of the pyrolytic gas sample and ambient air.

Ecological & Economic Evaluation

The overall GHG emission and cost of the 3 typical procedures were summarized (from spent battery to LFP final product) based on the typical procedures in **Table S4-S6**. All values of chemicals were calculated based on Chinese wholesale average market price surveyed in 2021/6 (relatively stable stage) and converted to USD by fixed exchange rate of 1USD=6.4CNY. Additionally, the alternative fuel source was also listed in these table (for example, coal is the cheapest fuel but has the highest CO_2e, while the electricity is the counter-example), the final values in blanket are concluded based on the cost of the median case (fueled by natural gas).

Table S4 Summarized cost and CO_2e of repairing 1t spent LFP via this method.

Material & Process	CO_2e (t)	Cost ($)	Notes and References
Spent LFP shipping	0.010	950	Calculated based on the Argonne GREET Model,[9] assumed 1.25t LFP black mass was collected locally and carried 480km through rail transportation.
Spent LFP extraction	0.111		All by physical process: 0.0886kWh/kg LFP cathode according to Ref.[10]
$LiNO_3$	-	920	(~87kg, ~9kg of lithium inventory)
Industrial sugar	-	5	
Mixing and drying	0.014	20	Assumed mixed by a 200L V-shape barrel industrial mixer for 10 runs (10*2000W*30min=10kWh) and briefly dried in 60°C oven (~7kWh)
Heating (12MJ)	**0.732 (LNG)** 1.669 (Coal) 2.748 (Electric)	70 (Coal) **200 (LNG)** 495 (Electric)	Analogical energy cost of LFP synthesis,[11] related CO_2e was calculated based on the fuel value: coal 29.3MJ/kg (7.99 MJ/kg CO_2e, ~$152/t) and natural gas 50.2MJ/kg (18.25 MJ/kg CO_2e, ~$0.5/m³) with 90% efficiency.
Tail gas treatment	0.053*	25	*Measured CO_2e by semiquantitative mass spectrometry analysis result.
Others	0.008	150	Analogical estimation of Ref. [12]
Total	0.928-2.944 **(0.928)**	2140-2565 **(2270)**	Electricity-related CO_2e were calculated based on the east China grid emission factor (0.809kg/kWh)

Table S5 Summarized cost and CO_2e of repairing 1t spent LFP via annealing method.

Material & Process	CO$_2$e (t)	Cost ($)	Notes and References
Spent LFP shipping	0.010		Same as the **Table S4**
Spent LFP extraction	0.111	950	
Li$_2$CO$_3$	-	770	(~49kg, ~9kg of lithium inventory)
Industrial sugar	-	15	
Mixing	0.008	10	Assumed mixed by a 200L V-shape barrel industrial mixer for 10 runs (10*2000W*30min=10kWh)
Annealing (30-54MJ)	1.826-**3.288** (LNG) 4.172-7.509 (Coal) 6.87-12.36 (Electric)	170-310 (Coal) 510-**920** (LNG) 1245-2250 (Elect.)	Analogical energy cost of LFP synthesis,[11] related CO$_2$e was calculated based on the fuel value: coal 29.3MJ/kg (7.99 MJ/kg CO$_2$e, ~$152/t) and natural gas 50.2MJ/kg (18.25 MJ/kg CO$_2$e, ~$0.5/m^3) with 90% efficiency.
Protective Gas	-	**230** (N$_2$) 565 (Ar/H$_2$)	4h*3600*2mL/s + 40L per 500g
Tail gas treatment	0.166	25	Estimated CO$_2$e of decomposing all Li$_2$CO$_3$, sugar and 1% of carbon residue.
Others	0.016	300	Analogical estimation of Ref. [12]
Total	2.137-12.67 **(3.599)**	2240-4655 **(3220)**	Electricity-related CO$_2$e were calculated based on the east China grid emission factor (0.809kg/kWh)

Table S6 Summarized cost and CO_2e of repairing 1t spent LFP via hydrometallurgical recycle (to Li_2CO_3) and re-synthesis (via $FePO_4$ route) process.

Material & Process	CO_2e (t)	Cost ($)	Notes and References
Spent LFP shipping	0.012	1140	Same as the **Table S4,** but cost more raw material (~1.5t) to extract ~0.24t Li_2CO_3 (with 95% leaching efficiency) for producing 1t LFP.
Spent LFP extraction	0.133		
H_2SO_4 (~0.75t)	-	150	H_2O_2 and other additives were omitted.
$FePO_4$ (~0.95t)	-	1630	Purchased as raw material for producing 1t LFP.
Fe_2SO_4 (~1.1t) (by-product)	-	-240	Assumed Fe_2SO_4 by-product was collected and sold to flocculant manufactor.
Filtration & Calcination	0.048 + 0.936 (LNG)	270	Pre-treatment to avoid HF release during leaching,[10] by annealing in LNG furnace.
Grinding & Leaching	0.058		Energy consumption: 0.036 and 0.0352 (kWh/kg) respectively, according to Ref.[13] Assuming the extracted salts were directly used as precursor without calcinated.[14]
Re-synthesis Annealing (60-105MJ)[11]	3.652-**6.393** (LNG) 8.341-14.60 (Coal) 13.73-24.03 (Electric)	470-725 (Coal) 1010-**1790** (LNG) 2630-5250 (Electric)	Related CO_2e was calculated based on the fuel value: coal 29.3MJ/kg (7.99 MJ/kg CO_2e, ~$152/t) and natural gas 50.2MJ/kg (18.25 MJ/kg CO_2e, ~$0.5/m^3) with 90% efficiency.
Protective Gas	-	410 (N_2)	8h*3600*2mL/s + 40L per 500g
Direct CO_2e	0.143	-	Estimated CO_2e of decomposing all Li_2CO_3.
Others	0.024	450	Analogical estimation of Ref. [12]
Total	5.006-25.38 **(7.747)**	4280-9060 **(5600)**	Electricity-related CO_2e were calculated based on the east China grid emission factor (0.809kg/kWh)

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