Supporting Information

A paired electrolysis approach for recycling spent lithium iron phosphate batteries in an undivided molten salt cell

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Roasting experiment: A tube furnace was used for performing the molten salt roasting flowed with Ar. First, the LiFePO$_4$ powder was mixed with pre-mixed Na$_2$CO$_3$-K$_2$CO$_3$ salt at a certain mole ratio ($\frac{n_{\text{LiFePO}_4}}{n_{\text{CO}_2\text{O}_3}} = 1: 2$), and then the mixture was ground together in a planetary ball mill for 4 h to ensure uniform mixing. Second, the well-mixed mixture was placed in tube furnace to conduct roasting. The temperature was raised to 750 °C at a heated rate of 5 °C min$^{-1}$ under the protection of Ar and then roasting for 2 h at 750 °C. Finally, after the tube furnace cooled down, the product was taken out and then washed with deionized water to remove the soluble salt. The product drying at 80 °C for 12 h was then characterized.

The mixture of LiFePO$_4$ powder and graphite powder was also roasted for 2 h at 750 °C under Ar atmosphere, and the mass ratio of graphite/LiFePO$_4$ was 2: 1. Besides, the LiFePO$_4$ powder was roasted for 2 h at 750 °C in air and in Ar, respectively.

Supplementary figures

Fig. S1 Current profiles of the electrolyzer with a graphite anode (a) and Ni10Cu11Fe anode (b) under different cell voltages.
Fig. S2 XRD patterns of electrolytic products obtained under different cell voltages adopting graphite as the anode (a) and Ni10Cu11Fe alloy as the anode (b).

Fig. S3 XRD patterns of electrolytic cathodic/anodic products obtained at three different types of molten salt electrolyzers with a LiFePO$_4$ cathode coupling with the same LiFePO$_4$ anode (a, b), a graphite anode (c), and a Ni10Cu11Fe anode (d).
Energy efficiency calculation

Under the cell voltage of 0.7 V, the weight of dual LiFePO$_4$ electrodes was 2.91 g, and the electrodes were completely reduced to solid Fe and oxidized to solid Fe$_3$O$_4$, respectively. And 1 mol of LiFePO$_4$ consumes 0.5 mol of electrons. The energy consumption ($E$) is calculated by equations S1 and S2:

$$E = U \times Q \quad \text{(S1)}$$

$$Q = n_e \times F \quad \text{(S2)}$$

where $U$ is the applied cell voltage, $Q$ is the consumed charge, $n_e$ is the mole of transferring electrons and $F$ is the Faraday constant.

$$Q = n_e \times F = \frac{1}{2} \times \frac{m_{\text{LiFePO}_4}}{M_{\text{LiFePO}_4}} \times F = \frac{1}{2} \times \frac{2.192}{157.76} \times 96485 \ A \cdot s = 889.87 \ A \cdot s$$

$$E = U \times Q = 0.7 \times 889.87 \ W \cdot s = 623.34 \ W \cdot h$$

According to the battery testing system, the recorded energy consumption ($E_r$) was 0.1929 W h. The energy efficiency ($\eta$) is calculated to 89.68% by equation S3.

$$\eta = \frac{E}{E_r} = \frac{0.173}{0.1929} = 89.68\%$$

(S3)

Economic evaluation

Assuming dealing with 1 kg of LiFePO$_4$ powder and the Li$^+$ recovery rate ($^{\text{rLi}}$) is 95.2%, the generated NaLi$_2$PO$_4$ mass ($m_{\text{NaLi}_2\text{PO}_4}$) can be calculated:

$$m_{\text{NaLi}_2\text{PO}_4} = \frac{m_{\text{LiFePO}_4}}{M_{\text{LiFePO}_4}} \times \frac{1}{2} \times M_{\text{NaLi}_2\text{PO}_4} \times 95.2\% = \frac{1000}{157.76} \times \frac{1}{2} \times 131.8 \times 95.2\% = 397.67 \ g$$

And the precipitated Li$_3$PO$_4$ mass ($m_{\text{Li}_3\text{PO}_4}$) also can be calculated:
\[ m_{Li_3PO_4} = \frac{m_{NaLi_2PO_4}}{M_{NaLi_2PO_4}} \times \frac{2}{3} \times M_{Li_3PO_4} = \frac{397.67}{131.8} \times \frac{2}{3} \times 115.7 = 232.73 \text{ g} \]

At the same time, the mass of generated Fe \((m_{Fe})\) and \(Fe_3O_4\) \((m_{Fe_3O_4})\) can be calculated as 88.74 g and 367.65 g, respectively.

On the assumption, the total mass of \(Na_2CO_3-K_2CO_3\) molten salt is 7 kg, and according to the molar ration (Na: K = 59: 41), the \(Na_2CO_3\) and \(K_2CO_3\) was weighed as 3672.46 g and 3327.54 g, respectively. The electrolysis was conducted under 0.7 V and the energy efficiency (\(\eta\)) is 89.68\%. Therefore, the power consumption is calculated:

\[
E = \frac{U \times Q}{\eta} = 0.7 \times \frac{1000}{157.76} \times \frac{1}{2} \times 96485 \div 89.68\% = 238690.62 \text{ W} \cdot \text{s} = 0.066 \text{ Kw} \cdot \text{h}
\]

The costs of \(Na_2CO_3\), \(K_2CO_3\), \(Li_3PO_4\), Fe powder and \(Fe_3O_4\) are 2.12 $/500g, 3.81 $/500g, 28.68 $/100g, 6.50 $/500g and 13.28 $/500g, respectively. And the price of electricity is 0.071 $/kW h. So, the total cost \((C_{total})\) and total profit \((P_{total})\) are calculated:

\[
C_{total} = C_{Na_2CO_3} + C_{K_2CO_3} + C_{electricity} = 3672.46 \times \frac{2.12}{500} + 3327.54 \times \frac{3.81}{500} + 0.066 \times 0.071 = 40.93 \text{ $} \\
P_{total} = P_{Li_3PO_4} + P_{Fe} + P_{Fe_3O_4} = 232.73 \times \frac{28.68}{100} + 88.74 \times \frac{6.5}{500} + 367.65 \times \frac{13.28}{500} = 77.67 \text{ $}
\]

Therefore, the total processing revenue \((P)\) can be obtained by treating 1 kg spent \(LiFePO_4\) powder with paired electrolysis process:

\[
P = P_{total} - C_{total} = 77.67 - 40.93 = 36.74 \text{ $}
\]

In summary, when dealing with 1 kg of spent \(LiFePO_4\) powders, the total profit of whole processes in this study is around 36.74 $.

Supplementary tables
**Table S1** Summary of reported approaches for recycling spent LiFePO$_4$ batteries.

<table>
<thead>
<tr>
<th>Recycling method</th>
<th>Chemical agents</th>
<th>Recovery rates</th>
<th>Products</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrometallurgy</strong></td>
<td>0.3 M H$_2$SO$_4$ (H$_2$O/Li molar ratio 2.07, H$_2$O$_4$/Li molar ratio 0.57, 60 °C, and 120 min), Na$_2$PO$_4$ as precipitant</td>
<td>Li 95.56%</td>
<td>FePO$_4$, 2H$_2$O and Li$_x$PO$_4$</td>
<td>1</td>
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<tr>
<td></td>
<td>0.8 M CH$_3$COOH as leaching agent, 6 vol% H$_2$O$_2$ as oxidant (S/L ratio of 120 g L$^{-1}$, 50 °C, 30 min), Na$_2$CO$_3$ as precipitant</td>
<td>Li 95.05%</td>
<td>FePO$_4$, Li$_2$CO$_3$</td>
<td>2</td>
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<td></td>
<td>0.5 M H$_3$PO$_4$ as leaching agent with LiFePO$_4$/H$_3$PO$_4$ molar ratio of 1:3:16, at room temperature and 1 h</td>
<td>FePO$_4$, 2H$_2$O and LiH$_2$PO$_4$</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EDTA-2Na as activation additive (cathode powder/EDTA-2Na mass ratio of 3:1, activation time of 2 h), 0.6 M H$_3$PO$_4$ as leaching agent (S/L ratio of 50 g L$^{-1}$, and leaching time of 20 min)</td>
<td>Fe 97.67%, Li 94.29%</td>
<td>FePO$_4$, 2H$_2$O and Li$_2$PO$_4$</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>2.5 M H$_2$SO$_4$ (L/S ratio of 10 mL g$^{-1}$, 60 °C, 4 h), NH$_3$:H$_2$O and Na$_2$CO$_3$ as precipitant</td>
<td>Li 97%, Fe 98%</td>
<td>FePO$_4$, Li$_2$CO$_3$</td>
<td>5</td>
</tr>
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<td></td>
<td>1.05 times theoretical amount of Na$_2$S$_2$O$_4$ as leaching agent and oxidation agent (S/L ratio 300 g L$^{-1}$, 25 °C, 20 min), Na$_2$CO$_3$ as precipitant</td>
<td>Li 99%</td>
<td>FePO$_4$, Li$_2$CO$_3$</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>4M HCl, 6 M NH$_3$, H$_2$O and Na$_2$PO$_4$ as precipitant</td>
<td>FePO$_4$, Li$_2$PO$_4$</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_2$SO$_4$ and H$_2$O as leaching agents, NaOH as precipitant, with LiFePO$_4$/H$_2$SO$_4$/NaOH molar ratio of 1:8:15</td>
<td>Fe 97.6%, Li 96.9%</td>
<td>Fe(OH)$_3$, FePO$_4$, 2H$_2$O, and Li$_2$PO$_4$</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>6 M HCl as leaching agent, 6.25% NH$_3$, H$_2$O as precipitant</td>
<td>FePO$_4$, 2H$_2$O</td>
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<td></td>
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<tr>
<td></td>
<td>heat-treatment cathode powders at 650 °C for 1 h under an Ar/H$_2$ flow</td>
<td>LiFePO$_4$</td>
<td>10</td>
<td></td>
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<tr>
<td><strong>Direct regeneration</strong></td>
<td>soaking cathode plates in DMAC solvent at 30 °C for 30 min</td>
<td>LiFePO$_4$</td>
<td>11</td>
<td></td>
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<tr>
<td></td>
<td>heating cathode scraps at 400–600 °C for 30 min under N$_2$</td>
<td>LiFePO$_4$</td>
<td>12</td>
<td></td>
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<tr>
<td><strong>Mechanochemistry</strong></td>
<td>NaCl as cogrinding reagent at room temperature, Na$_2$CO$_3$ as precipitant</td>
<td>NaFePO$_4$, Li$_2$CO$_3$</td>
<td>13</td>
<td></td>
</tr>
<tr>
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<td>oxalic acid as cogrinding reagent and water leaching</td>
<td>Fe 94%, Li 99%</td>
<td>FeC$_2$O$_4$, 2H$_2$O and Li$_2$PO$_4$</td>
<td>14</td>
</tr>
<tr>
<td><strong>Electrochemical method</strong></td>
<td>0.20 M K$_2$[Fe(CN)$_6$] as selective and regenerative redox mediator at a constant current of 5 mA cm$^{-2}$</td>
<td>FePO$_4$, LiOH</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>
Table S2. The environmental impact comparison of different methods for spent LiFePO$_4$ batteries.

<table>
<thead>
<tr>
<th>Method</th>
<th>Operating condition</th>
<th>Waste generation</th>
<th>Energy source</th>
<th>Environmental footprint</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrometallurgy</td>
<td>Mild</td>
<td>Wastewater and waste gas</td>
<td>Chemical agents</td>
<td>Severe</td>
</tr>
<tr>
<td>Regeneration</td>
<td>High temperature</td>
<td>Less waste</td>
<td>Heat</td>
<td>Medium</td>
</tr>
<tr>
<td>Mechanochemistry</td>
<td>Mild</td>
<td>Less waste</td>
<td>Chemicals and ball-milling</td>
<td>Medium</td>
</tr>
<tr>
<td>Molten-salt paired electrolysis</td>
<td>Medium-high temperature</td>
<td>Partial waste gas</td>
<td>Electrons</td>
<td>Medium</td>
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</table>

References


