

Supporting Information for:

Upcycling of LiFePO_4 to High-Performance $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$: Activating the Mn Redox Platform for Stable Energy Storage

Zihao Zeng^{a#}, Xuepeng Qi^{a#}, Wei Sun^a, Peng Ge^a, Yue Yang^{a}*

^a School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

* Corresponding authors: Prof. Dr Yue Yang.

E-mail: yangyue18@csu.edu.cn; Eric1911@126.com

These authors contributed to this work equally and should be regarded as co-first author.

System boundary and functional unit for economic analysis

The analysis starts from 1 kg of spent LFP cathode material and ends at the recovered/upcycled product. For pyrometallurgy: mixed metal alloy; for hydrometallurgy (Hydro): Li_2CO_3 and FePO_4 ; for this work (upcycling): LMFP. Collection, transportation, and pre-dismantling are excluded because they are identical for all three processes.

Calculated manners for economic analysis

The life-cycle and economic analysis is based on the functional unit of 1 kg of spent LFP cathode black mass after dismantling and separation from the aluminium foil. Total energy consumption (MJ per kg input) is the sum of three components: embedded energy in raw materials (materials), direct electricity or fuel used during the process (energy), and energy attributed to auxiliary operations such as off-gas treatment, wastewater handling, or process. Greenhouse gas emissions are calculated by multiplying the electricity consumption by the national average grid emission factor and adding the literature-based emissions from material inputs and process-specific chemical reactions. Economic revenue is obtained by multiplying the experimentally determined or literature-derived product yield (kg product per kg input) by the current market price of the final recovered/upcycled product (mixed metal alloy for pyrometallurgy, lithium carbonate plus iron phosphate for hydrometallurgy, and LMFP for the upcycling route). All three routes are compared under identical system boundaries, excluding collection, transportation, and dismantling. Key assumptions (e.g., lithium recovery yields, product yields, and emission factors) are explicitly stated, and sensitivity analyses are performed by varying electricity price, lithium carbonate price, and grid emission factor to test the robustness of the conclusions.

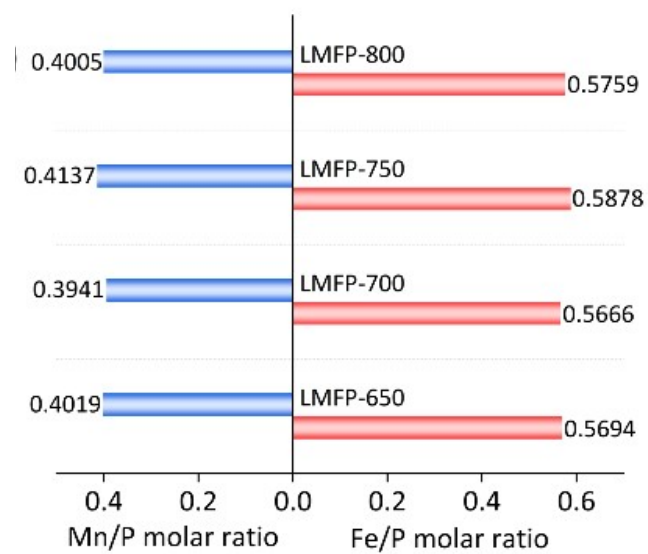


Figure S1. Molar ratio of transition metal elements (Fe/Mn) to P elements.

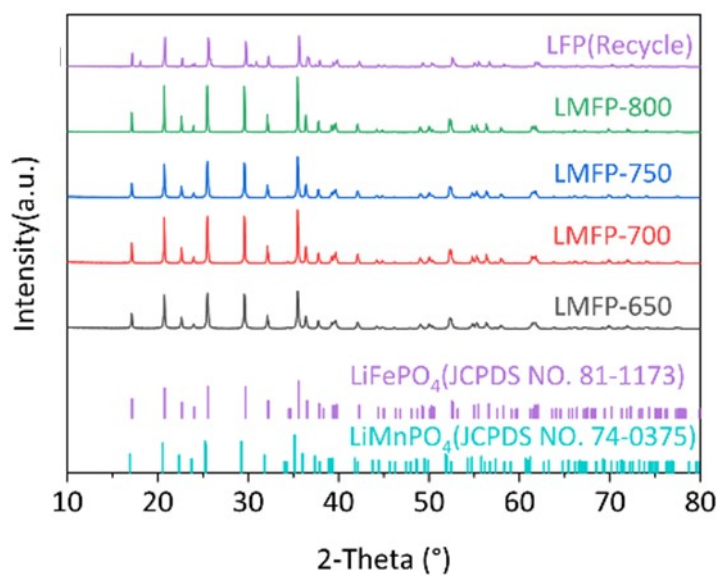


Figure S2. XRD patterns for LMFP-650, 700, 750, and 800 materials in the 2 theta regions of 15°–65°.

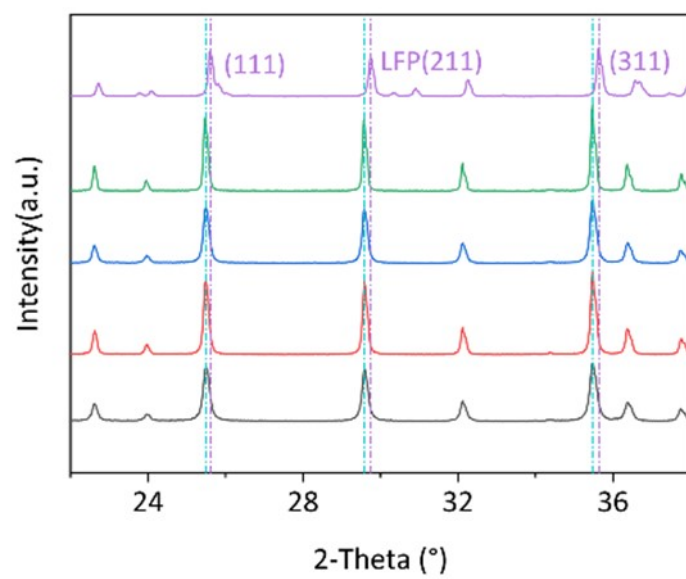


Figure S3. XRD patterns for LMFP-650, 700, 750, and 800 materials in the 2 theta regions of 22°–38°.

Table. S1 Data sources of economic analysis.

| Data type | Pro | Hydro | This work |
|---------------------------------|-------------------|------------------------------------------|-----------|
| Total energy consumption(MJ/kg) | 1.05 | 1.29 | 0.46 |
| GHG emissions (kg /kg) | 1.89 | 1.52 | 1.25 |
| Revenue (\$/kg) | 2.91 | 0.37 | 7.51 |
| Main product | Mixed metal alloy | $\text{Li}_2\text{CO}_3 + \text{FePO}_4$ | LMFP |

Table. S2 Materials Price of economic analysis.

| Material | Price (USD/kg) |
|------------------------------------------------------------------|-----------------------|
| Spent LFP cathode black mass | 3.44 |
| $[\text{Mn}(\text{CH}_3\text{COO})_2] \cdot 4\text{H}_2\text{O}$ | 0.83 |
| Glucose | 0.51 |
| Ethanol | 0.80 |
| H_2SO_4 | 0.10 |
| NaOH | 0.42 |
| LiOH | 22.22 |
| $\text{NH}_4\text{H}_2\text{PO}_4$ | 0.76 |

Table. S3 Product yield of economic analysis.

| parameter | Pro | Hydro | This work |
|------------------------|------|-------|-----------|
| Lithium recovery yield | <50% | >90% | ~100% |
| Product yield | 0.83 | 0.85 | 0.95 |

Table. S4 Energy prices of economic analysis.

| Energy Type | Price |
|-------------|---------------|
| electricity | 0.088 USD/kWh |
| water | 0.68 USD/ton |