Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

A sustainable strategy for spent Li-ion battery regeneration: microwave-hydrothermal relithiation complemented with anode-revived graphene to construct $LiFePO_4$/MWrGO cathode material

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Supporting information

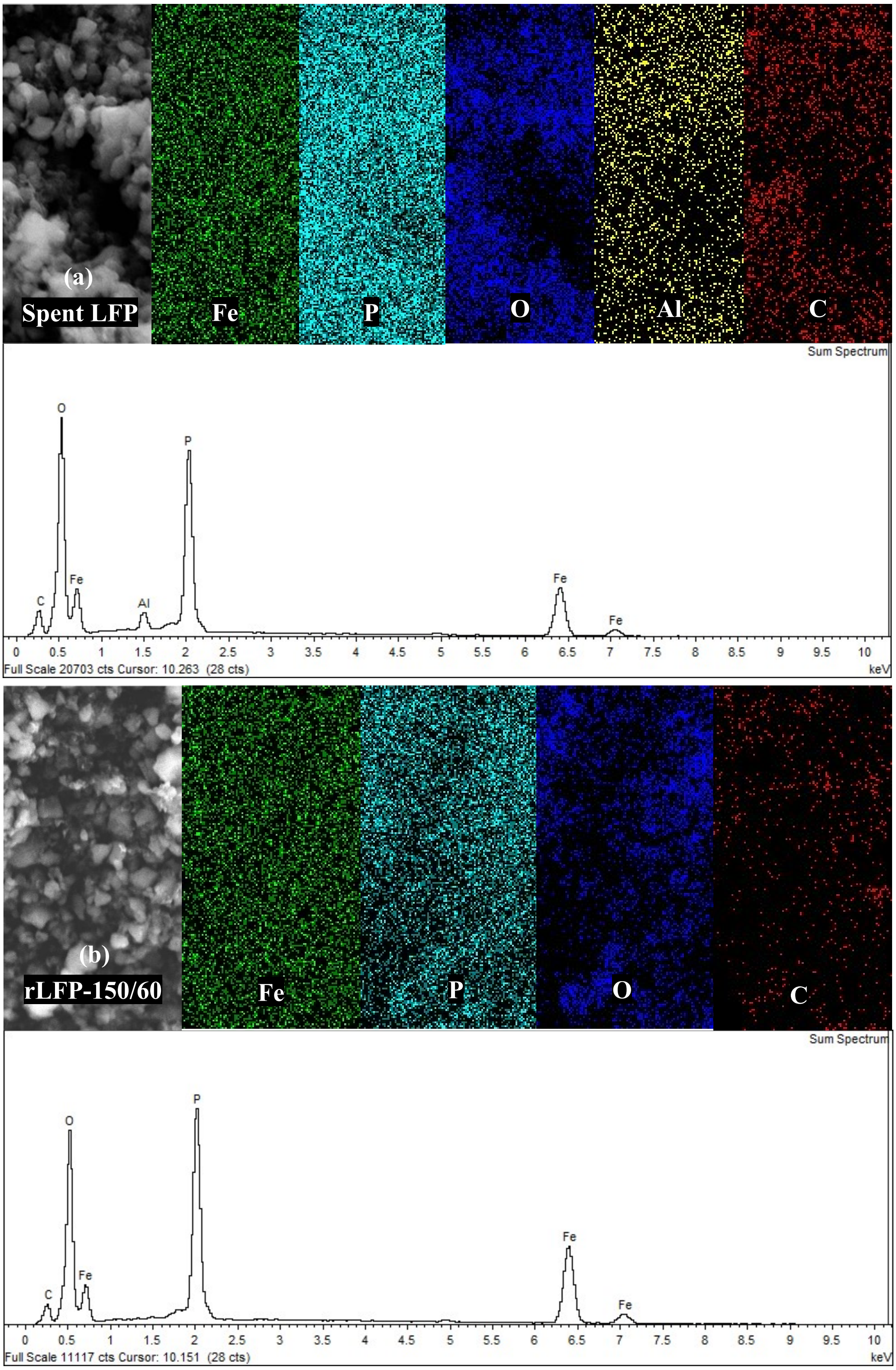


Fig. S1. The elemental composition and SEM-EDS mapping results of spent LFP and rLFP-150/60.

In order to investigate the coupling effect of microwave on the hydrothermal reduction process of LFP, the microwave-absorbing performance of spent LFP was tested in particular. It can be seen from **Figure S2** that the microwave absorption capacity of the spent LFP gradually increases with the increase of its dielectric loss tangent and magnetic loss tangent, and tends to be stable. Under the commonly used microwave radiation frequency of 2.45GHz, the dielectric loss tangent of LFP is approximately 0.35, and the magnetic loss tangent is about 0.5. Therefore, it can be deduced that LFP has certain microwave absorbing properties, which can better couple microwave energy to promote the hydrothermal reduction reaction and the lithium replenishment process.

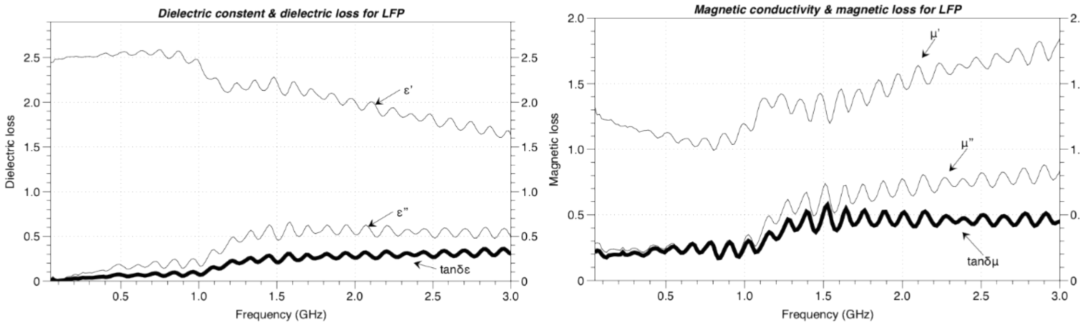


Fig. S2. Dielectric property test of spent LFP.

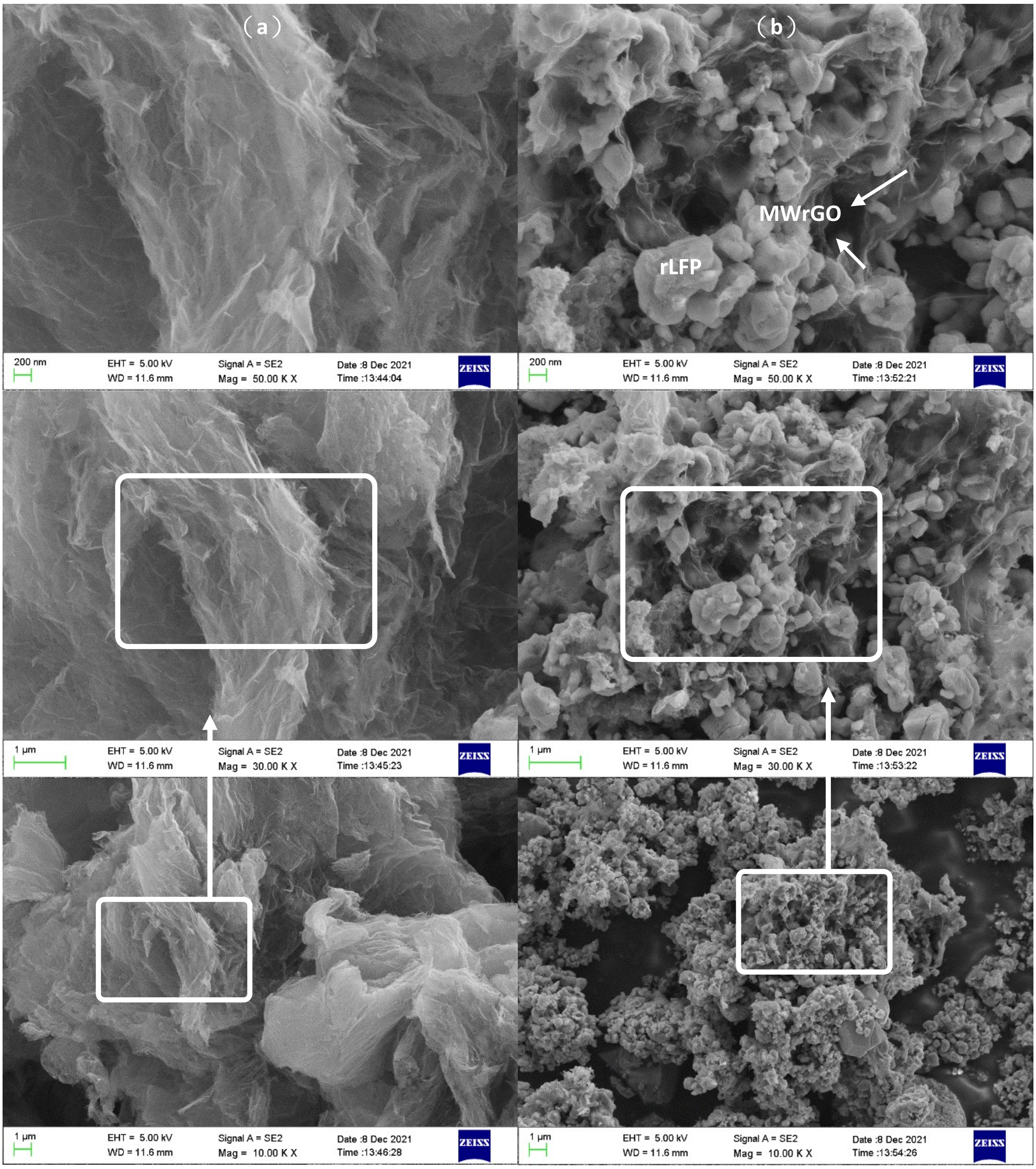


Fig. S3. Different magnification of SEM images for the transition state between spent LFP and MWrGO during the MWHT regenerating process.

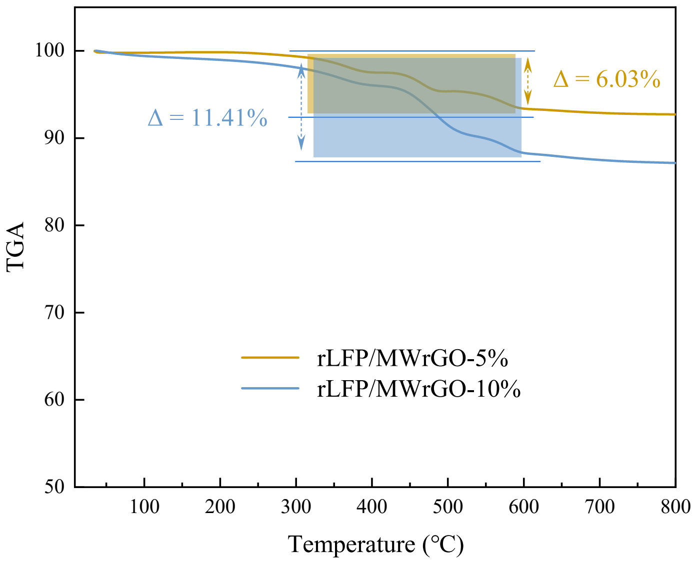


Fig. S4. TGA analysis of regenerated LFP/MWrGO composites.

Table S1. Summary table of the capacity retention ratios*.

The capacity retention ratios of the LFP cathodes regenerated under different conditions

Conditions	150 °C 30 min	150 °C 60 min	150 °C 120 min	150 °C 150 min	120 °C 60 min	180 °C 60 min
After 100 cycles	95.4 %	95.8 %	96.3 %	94.9 %	92.0 %	unstable
After 200 cycles	73.4 %	93.3 %	94.1 %	91.8 %	88.6 %	unstable

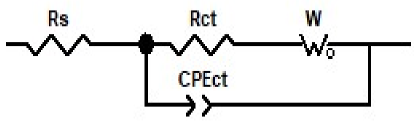
The capacity retention ratios of the LFP cathodes regenerated with different MWrGO dosage

Samples	rLFP	rLFP/MWrGO-1%	rLFP/MWrGO-5%	rLFP/MWrGO-10%
After 50 cycles	96.7 %	97.6 %	100 %	99.9 %
After 100 cycles	90.2 %	92.6 %	94.9 %	100 %

**The capacity retention rate of the Nth circle is obtained by dividing the specific capacity of the Nth circle by the specific capacity of the third circle, since the initial capacity is affected by battery activation.*

Table S2 EIS parameters of LFP materials from equivalent circuit fitting of experimental data

Samples	R_s (Ω)	R_{ct} (Ω)
Spent LFP	2.959	276.6
rLFP	2.261	288.6
rLFP/MwrGO-5%	2.314	84.1



Economic and environmental analysis:

Taking 1.0 kg of spent LFP batteries as the recycling object, a lab-scale economic evaluation based on our proposed MWHT regeneration strategy was carried out. In order to better demonstrate its economic advantages, a comparison focusing on the economic input and output in each process was also made among our work, the conventional hydrothermal method, and the improved hydrometallurgical method. As shown in **Figure 14**, the entire recycling process is mainly subdivided into four processes: dismantling, pretreatment, leaching, and regeneration. Since this work and the conventional hydrothermal method are both classified as direct regeneration strategy, their leaching steps are skipped. *Besides, note that there are no obvious differences in the treatments such as washing, drying, and grinding in the pretreatment and regeneration processes of all three methods, so the comparative analysis of this part of the economic investment has been weakened.*

The **water charge** of Jinan China involved below refers to the charge standard from Jinan Water Group Co, Ltd. (*https://www.jnwater.com.cn/*), about $ 0.651/m^3 ($ 1 = 1 US dollar = 6.4533 RMB), including basic water price ($ 0.434), water resource fee ($ 0.062) and sewage treatment fee ($ 0.155). The **electricity bill** of Jinan China refers to Shandong Power Grid Sales Electricity Price List (2021) from State Grid Shandong Electric Power Company (*http://www.sd.sgcc.com.cn/*), about $ 0.1313/kWh. The prices of all reagents are based on the price lists from Sinopharm Chemical Reagent Co., Ltd. (*https://www.reagent.com.cn/*) and Shanghai Macklin Biochemical Co., Ltd. (*http://www.macklin.cn/info*), and the economical ones are selected.

According to **Figure 14**, the **green** text represents input parameters (including the quality and price) and the **red** text represents output and revenue. Detailed descriptions are as follows:

1. Dismantling: The **1.0 kg** of LFP battery (provided by Shandong Jiuli Electronic Technology Co., Ltd., China) were dismantled after deep discharge, and approximately **390 g** of cathode sheets (i.e., Al foils with LFP cathode material attached) can be obtained. The input cost of **1.0 kg** spent LFP batteries totted up to **$ 0.5**.

In our work, about **390 g** of anode sheets were also recycled.

2. Pretreatment: Before further processing the LFP cathode material, it is necessary to dissociate it from the Al foil as we mentioned in the Experimental Method. The separation methods mainly include pyrolysis (heat treatment) and hydrolysis (NaOH dissolution or solvent dissolution). In our work, since the recycled cathodes were bonded by water-based binder, water hydrolysis was employed with the assistance of ultrasonication. The whole separation process is energy-efficient and environmental-friendly because the low-power (**0.2 kW**) ultrasonic treatment shortens the processing time from more than 6 hours to 1 hour, greatly improved the dissolving efficiency. Also, water as the solvent does not produce GHGs. The input cost of water (**~3.9 L**) in the process is **$ 0.0025**, and the ultrasonic treatment lasts 1 hour with the power of **0.2 kW**. Therefore, the cost of the ultrasonic hydrolysis pretreatment amounts to **$ 0.028**, and the same energy consumption goes for **390 g** of anode sheets.

   Our work also involves the upgrade of anode graphite and its application to the modification of regenerated LFP, so a further processing is required. According to the quantity of obtained spent LFP, **20 g** of recovered graphite is selected for upgrade, undergoing processes such as Hummer's method (reagent input: **$ 5.4729**), overnight freeze drying (energy consumption: **$ 4.2541**) and **5 seconds** of microwave reductive exfoliation (energy consumption: **$ 0.0002**). In order to dope LFP with **5%** MWrGO to improve its conductivity, **15.5 g** of the MWrGO is electrostatically self-assembled into the cathode via surface charge modification (reagent input: **$ 0.0001**), and the remaining **4.5g** is used as a backup with an extremely high bonus, over a few thousand dollars (refer to the market price of **$ 825.375/g**). In a conventional hydrothermal method, according to reported experiments, NMP was used as an organic solvent to treat the LFP anode containing oil-based binder. Based on the price list, NMP is relatively expensive (**$ 0.022/mL**) and its consumption is not small according to the solubility of **200 g/L**, which costs about **$ 3.235**. It thus appears that the application of green binder is not only beneficial to environmental protection, but also can reduce the investment in recycling. In the improved hydrometallurgical method, NaOH dissolution was selected to pretreat the cathode sheets, and the basic solution is effective for any kind of binder. It is simple and crude, but will produce liters of waste liquid. To prevent the dissolution of Al foil, the whole process consumes about **90 g** of NaOH (**$ 0.0078/g**) and **7.8 L** of water, so the total cost adds up to **$ 0.698**.

3. Leaching: Our work (MWHT regeneration) and the conventional hydrothermal method are both classified as direct regeneration strategy, which skips the leaching step. Since leaching is an exclusive step to the hydrometallurgical method, it needs to consider the additional costs from treatments like washing (**$ 0.0039**), drying (**$ 1.5756**) and grinding (**$ 0.47268**). The improved hydrometallurgy uses a combination of green organic acid acetic acid (HAc) (**0.8 mol/L**) and H_2O_2 (**6 vol.%**) for the leaching of waste LFP. The application of the organic acid greatly reduces the environmental pollution caused by conventional methods. Based on the reported optimum experimental conditions (solid-to-liquid ratio: **120 g/L**; heating mode: **50 °C/30 min/0.5kW**), the cost of reagents (HAc **$ 0.0062/mL** and H_2O_2 **$ 0.0068/mL**) invested in the process is **$ 0.732 + $ 1.057 = $ 1.789**, the water fee is **$ 0.0015**, and the electricity bill is **$ 0.0328**. Therefore, the total input of improved leaching amounts to **$ 3.875**.
4. Regeneration: In our work, $LiOH\cdot H_2O$ (**$ 0.0546/g**) and L-ascorbic acid (AA) (**$ 0.2413/g**) were selected as a lithium source supplement and a reducing agent. Since the unique thermal effect of microwave heating greatly promotes the hydrothermal regeneration, it is found that the expected repairing purpose can be easily achieved at the molar ratio of LFP:LiOH:AA=**1:1:0.5**. The regenerating solution can be recycled, so in theory, the entire

proposed process does not produce waste water. On this basis, the reagent volume is multiplied by **80%** to reduce waste and improve atomic economy, considering that LFP is not **100%** lithium-deficient and when a closed-loop MWHT regeneration is performed, there will be a certain amount of residue in every cycle. In this way, it contributes to the total reagent input of **$ 10.256**. Microwave ChemStation (MDS-6G, SINEO, Shanghai) was employed to regenerate LFP under the optimum conditions (**0.4 kW, 150 °C, 1 h**). The total energy input of MWHT process costs **$ 0.0525** and the water fee amounts to **$ 0.0040**. In the MWHT regeneration, at least **310 g** of LFP that can be readily used in new batteries was regenerated, with a total value of more than **$ 132.618** (The market price of LFP is **$ 0.4278/g**). Meanwhile, AA loses electrons during regeneration and decomposes into H_2O and by-product dehydroascorbic acid (DHAA), which has a certain effect as an antioxidant precursor in the field of pharmaceutical preparation and can be recycled from the residual liquid to further increase the revenue generated from recycling. Since the residual liquid contains few impurities, the crudely extracted DHHA is expected to obtain a profit of **0.1%** of the price of DHHA on sale (**$ 0.3825/g**), providing a considerable reward of **$ 105.876**. When **15.5 g** of upgraded MWrGO is added into the regeneration process, the output of LFP/MWrGO-5% will reach about **325.5 g**, with a total value of more than **$ 139.249**. Besides, the regenerated LFP/MWrGO-5% is predicted to own an even higher value in the market context where high performance is pursued, and **4.5g** of conductive MWrGO as a spare is also extremely valuable because it sells for over **$ 825.375/g**. Compared with the MWHT regeneration, the conventional hydrothermal method is a bit more wasteful in terms of reagent input. According to the reported literature, a highly concentrated regenerating solution is required, where the molar ratio of LFP:LiOH:AA:SDBS = **1:3:3:1,** contributing to a considerable cost of **$ 47.542**. The water fee is **$ 0.0040**. Although the addition of surfactant SDBS avoids particle agglomeration, it brings a certain pollution and also increases the difficulty of extracting the by-product DHAA. According to previous work, regarding the energy consumption, conventional hydrothermal also requires a higher power (**~1 kW**) and a longer reaction time (**6 h**) with an electricity cost of **$ 0.7878**. Assuming that the conventional hydrothermal process can also regenerate all the input LFP without loss, that is, the product profit reaches **$ 132.618**. Regarding the improved hydrometallurgical treatment, $FePO_4$ and Li-containing solution were obtained by acid leaching, with the leaching rate of Li, **84.76%** and the recovery rate of $FePO_4$, **99.07%** based on the reported experiment. The solution needs to be further neutralized and precipitated with an input of about **82.67g** of NaOH, costing about **$ 0.5894**. Thus, after filtration, washing, drying and grinding (a total cost of **$ 2.052**), about **61.53g** of Li_2CO_3 and **293.60g** of $FePO_4$ can be acquired. Compared with the direct regeneration strategy, the main elements are inevitably lost during the acid leaching and precipitation process. Theoretically, an additional Li_2CO_3 (**~10.14 g**) and oxalic acid (**90.83 g**) are needed during the regeneration of LFP, and the output of LFP reaches **306.5 g**, with the value of **$ 130.930**.

5. On the whole, compared with the conventional hydrothermal and the improved hydrometallurgical treatment, our work (MWHT regeneration) can reap the greatest total profit (rLFP **$ 121.777** and rLFP/MWrGO **$ 118.653**), with not only the largest regeneration of cathode from **1.0 kg** of LFP batteries, but also the high value-added by-products (rough DHAA and extra MWrGO). Besides, the input and output of each process are estimated based on the material balance under ideal experimental conditions, and when it comes to industrial applications, the issues such as labor costs, site rent, and equipment cost also need to be taken into consideration. In this way, MWHT regeneration demonstrates a great advantage in controlling labor costs as well because it greatly shortens the labor hours. In summary, MWHT has great potential in the industrial application of lithium-ion battery cathode material recycling, which can save more investment and obtain

higher returns.

Reference

Local water charge list (Jinan, China) from:

https://www.jnwater.com.cn/custom/ysjg.html

Local electricity bill list (Jinan, China) from:

http://www.sd.sgcc.com.cn/html/main/col2752/202109/18/20210918120931148303528_1.html

All reagents are based on the price lists from:

https://www.reagent.com.cn/ and http://www.macklin.cn/info