Supplementary Materials for

A green and sustainable strategy toward lithium resources recycling from spent batteries

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- Figs. S1 to S26
- Tables S1 to S4
- Note S1
- Legend for movie S1

Other Supplementary Material for this manuscript includes the following:

- Movie S1
Fig. S1. The structure charts of the roll-to-roll lithium recycling system. A. The anode part of the lithium recycling device. B. The cathode part of the lithium recycling device. C. Top view illustration of the lithium recycling system.

The anode part of the lithium recycling device comprises a roller for winding the lithium-containing electrode of spent batteries and a drive shaft which is fixed at the bottom of the roller and made of insulating materials; the roller across through the top cover of the drying box and a conductive slip ring which connected with the positive terminal of the battery test machine is arranged between the roller and drying box; the driving shaft across the drying box and connect with the asynchronous motor through the electromagnetic clutch.

The cathode part of the lithium recycling device includes the LLZTO ceramic tube and two limit plates which are made of insulating material are arranged in the top and bottom of the LLZTO ceramic tube body. An upper pipe and a bottom pipe are connected with the inner cavity of the LLZTO ceramic tube; the upper tube across through the bearing, rotating joint and connected with
pipelines that are linked with the deionized water storage tank and hydrogen recovery tank; the bottom pipe installed on the bearing of the drying box across through the rotating joint and solenoid valve to connect with the lithium hydroxide recovery tank; the platinum electrode is fixed in the cavity of the LLZTO ceramic tube. The top side of platinum electrode passes through the pipe, rotating joint and is connected with the negative terminal of the battery test machine. From the top view of the lithium recycling system, we can see under the driving of asynchronous motor, spent electrode after lithium selectively recycling through the LLZTO@LiTFSI+P3HT can achieve roll-to-roll recovery.
**Fig. S2. Schematic procedure for the H$_2$ gas capture design based on our recycling system for spent LIBs.**

As for the H$_2$ gas capture design, considering the cathode reaction process is associated with the coexistence of liquid and gas, the produced H$_2$ inevitably contains water, so the produced H$_2$ firstly goes through the separation and purification device to remove a large amount of water by cryogenic freezing, then enters into a drying device to ensure the fully absorbance of the remaining water. Afterwards, the treated H$_2$ gas moves to a buffer tank that connected to a hydrogen compressor, the compressed high-pressure H$_2$ finally enters into the H$_2$ storage tank for further green energy utilization.
Fig. S3. The XRD patterns of bare LLZTO immersed in different aqueous solutions for one month.

It is clear to see that the cubic structure of LLZTO does not destroy after immersed in various aqueous solutions.
Fig. S4. EIS of LLZTO pallet immersed in different aqueous solutions for one month.

The ion conductivity of bare LLZTO experience greatly degrade after immersed in the aqueous solutions.
Fig. S5. The photograph of P3HT film. A. Pure P3HT film. B. P3HT film immersed in water.
Fig. S6. Dynamic water contact angle of pure P3HT film.
Fig. S7. The stability of P3HT freestanding structure. A. Fresh P3HT film. B. 2 months after
Fig. S8. TGA thermograms of P3HT.

This result identifies P3HT is very stable in the working temperature (45°C) of the lithium recycling system.
Fig. S9. The EIS of the H-type cell with the rubber mat as separator.

Because the rubber mat is an ionic insulator, lithium ion cannot diffuse through it in the LiOH solution, so its EIS spectrum is disordered.
Fig. S10. Electrochemical model for EIS in Fig.2E
Table S1 Parameter identification for EIS in Fig.2E

|             | R1 $R_{ct}$/ Ω | CPE1 | R2 $R_c$/ Ω | CPE2 |
|-------------|----------------|------|--------------|------|
| P3HT+LiTFSI film | 843            | 7.1×10^{-5} | 0.91         | 241  | 8.3×10^{-5} | 0.76 |
| None separator | —               | —    | —            | 30   | 8.2×10^{-5} | 0.76 |
Fig. S11. Dynamic water contact angle LLZTO before and after P3HT modification. A. Dynamic water contact angle of bare LLZTO pallet. B. Dynamic water contact angle of LLZTO@LiTFSI+P3HT pallet.

It is clear that the P3HT modification adjusts the original hydrophilic LLZTO to be hydrophobic.
Fig. S12. Photos of LLZTO@LiTFSI+P3HT ceramic electrolyte tube before and after immersing in water for two months.
Fig. S13. SEM image of A. pristine LLZTO and B. LLZTO after immersing in distilled water for one month.

The amorphous grain-boundary phase of pristine LLZTO is ascribed to LiAlO$_2$. We can see the side product Al(OH)$_3$ shows up in the LLZTO after immersing in water for one month. As for reason, the LiAlO$_2$ is unstable in water, which usually causes the following reaction: $2\text{LiAlO}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + \text{Li}_2\text{O}$
Fig. S14. EDS of bare LLZTO tube immersed in distilled water for one month (scale bars: 10\(\mu\)m).
Fig. S15. SEM image of LLZTO@LiTFSI+P3HT after immersing in water for one month.

The P3HT modification on the surface of LLZTO successfully prevents the H⁺/Li⁺ exchange between LLZTO and H₂O, it is notable that the Al(OH)₃ with flake morphology does not show up in the grain boundary of LLZTO after immersing in water for one month.
Fig. S16. Computational model of LLZTO bulk and (010) surface. A. LLZTO with a formula \( \text{Li}_{51.2}\text{La}_{24}\text{Zr}_{11.2}\text{Ta}_{4.8}\text{O}_{96} \) through factional occupancy. The atom ratio is consistent with our experiments (\( \text{Li}_{6.4}\text{La}_{3}\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12} \)). B. Slab model for (010) surface with \( \text{Li}_{39}\text{La}_{18}\text{Zr}_{9}\text{Ta}_{3}\text{O}_{72} \), leading to an atomic ratio \( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12} \), being close to experimental result. Aquamarine and blue polyhedrons indicate \( \text{ZrO}_6 \) and \( \text{TaO}_6 \) units.
Fig. S17. Li extraction evaluation. ICP-OES measured content of Li, Fe elements in A. the LiFePO$_4$ electrode and B. catholyte before and after Li extraction based on the LLZTO@LiTFSI+P3HT roll-to-roll recycle system. The error value denotes the standard deviations from three times measurements for each sample.
Fig. S18. Li extraction evaluation. ICP-OES measured content of Li, Fe elements in A. the LiFePO$_4$ electrode and B. catholyte before and after Li extraction based on the LLZTO roll-to-roll recycle system. The error value denotes the standard deviations from three times measurements for each sample.
Fig. S19. Final product characterization. A. White powder obtained by evaporating the concentrated catholyte solution. B. the XRD pattern of the white powder.

The quantitative elemental analyses show that the purity of LiOH was 99.94%± 0.03%, and the weight percentages of Fe, La, Zr, and Ta in the product were 0.93 ± 0.30, 0.99 ±0.02, 2.16 ± 0.02, and 3.18 ± 0.01 ppm, respectively.
Fig. S20. The performance of lithium extraction system for LiFePO$_4$ electrode with distilled water as wetting agent A. The Li extraction profiles for lithium extraction system with distilled water as wetting agent. B. ICP-OES measured content of Li, Fe elements in the LiFePO$_4$ electrode from our lithium extraction system with distilled water as wetting agent. The error value denotes the standard deviations from three times measurements for each sample.
Fig. S21. XPS spectra of an NCM523 electrode during the Li extraction process. A. Ni 2p spectrum. B. Li 1s spectrum.

The analysis of high-resolution XPS spectra of Ni 2p\textsubscript{3/2} illustrates a chemical shift to higher binding energies with an increasing delithiation degree, evidencing the gradual oxidation of Ni due to the extraction of Li. The Ni 2p spectrum has 2p\textsubscript{3/2} and 2p\textsubscript{1/2} spin-orbit levels at 856.5 and 872.9 eV, respectively. As the Li extraction process proceeding, the peak intensity of Ni\textsuperscript{2+} obviously decreased, while the characteristic peak of Ni\textsuperscript{3+} shows an increasing trend. Particularly, the Ni 2p\textsubscript{3/2} and Ni 2p\textsubscript{1/2} peaks shift to lower binding energies at the end of Li extraction, which can be ascribed to the possible formation of Ni\textsuperscript{4+}.\textsuperscript{38} The Li 1s peak manifests the intensity of the peaks (55.9 eV) decreases with the increasing amount of Li extracted from the NCM523 electrode. Therefore, the extraction of lithium leads to valence changes via increased Ni\textsuperscript{3+} and decreased Ni\textsuperscript{2+}, which keeps the overall charge balance in the de-lithiated structures.
Fig. S22. TOF-SIMS depth profile of the fresh NCM523 electrode.
Fig. S23. XRD patterns of the LCoO$_2$ electrode before and after Li extraction.
Table S2. Satellite Relative Area (%) and Full Width at Half Maximum (eV) of the Main Peak from Co 2p$^{3/2}$ Spectra of LCO Electrode after Li Extraction.

|                          | % sat. area | fwhm (eV) |
|--------------------------|-------------|-----------|
| LiCoO$_2$ (LCO) electrode| 9.0         | 1.8       |
| LCO electrode after Li extraction | 4.6         | 3.1       |
Fig. S24. XPS spectra of a LCO electrode during the Li extraction process.

We observed a strong broadening of the main peak toward higher binding energies upon lithium extraction of LCO electrode. This observation can be attributed to the oxidation process of Co$^{3+}$. 
**Note S1. Detailed information for the cost assessment of spent LiFePO$_4$ battery lithium recovery**

Taking 1.0 kg of spent lithium iron phosphate (LiFePO$_4$) batteries as an example, the economic assessment for spent LiFePO$_4$ battery recovery was performed based on our proposed process. Materials balance and cost assessment of the integrated and designed procedure are shown in Fig. 6. The details are as follows (1$ = 6.3$ RMB):

i) Fig. 6 shows the separation of LiFePO$_4$ battery: 450 g LiFePO$_4$ cathode electrode, 50 g Cu foil, 35 g shell, and 100 g separator were obtained after a manual dismantling and sorting process. The input cost of 1.0 kg spent LiFePO$_4$ battery was $1.0, and the profits from the Cu foil and shell were $0.25 and $0.007, respectively. The prices for the spent LiFePO$_4$ battery ($1.0$/kg), shell ($0.2$/kg), Cu foil ($5.0$/kg) were provided by Huaxin Environmental Co. Ltd, Beijing, China.

**Table S3.** Material cost for a LLZTO tube with an inner diameter of 30mm, a length of 100mm and a wall thickness of 1.5mm.

| Raw materials | Mass   | Unit Price ($/g$) | Total price ($) |
|---------------|--------|-------------------|-----------------|
| La$_2$O$_3$   | 141.69 | 0.029             | 4.109           |
| Li$_2$CO$_3$  | 94.39  | 0.014             | 1.321           |
| ZrO$_2$       | 49.46  | 0.007             | 0.346           |
| Ta$_2$O$_5$   | 38.45  | 0.100             | 3.845           |
| Al$_2$O$_3$   | 3.67   | 0.007             | 0.025           |
| **LLZTO tube** | **287.32** | **0.03**     | **9.646**       |

ii) Fig. 6 includes the materials cost for LLZTO preparation, the initial cathode solution cost for the LiOH enrichment and the electricity cost for lithium recycling from 1.0 kg spent lithium iron phosphate (LiFePO$_4$) batteries. First, the cost for a LLZTO tube with an inner diameter of 60mm, a length of 200mm and a wall thickness of 1.5mm was calculated to be around $9.646. It is only one-time investment because each LLZTO@P3HT+LiTFSI membrane can be used for more than 100 times for lithium recycling. Therefore, the average cost for LLZTO@P3HT+LiTFSI membrane in each time spent battery recycle is around $1.41 which also includes the cost for anhydrous chloroform and anhydrous acetonitrile, P3HT and LiTFSI. The price for P3HT ($150/g) was provided by P-OLED Technology Co. Ltd, Xi’an, China. The price
for LiTFSI ($6.3/g), anhydrous chloroform ($8.5/L), anhydrous acetonitrile ($29/L), LiOH·H₂O ($151/kg) were obtained from the [https://www.sinoreagent.com/](https://www.sinoreagent.com/)

Second, the initial cathode solution for LiOH enrichment is 300 mL pure water with 20mg LiOH dissolve in to ensure the Li⁺ conductivity in the beginning recycling, the cost for this initial LiOH solution is $3.02.

iii) According to the Equation in Figure 1, about 60.75 g LiOH and 2.53 g H₂ were harvested. Therefore, 134.13 g Na₂CO₃ was needed to precipitate Li⁺ in the solution, and 93.5 g Li₂CO₃ was produced according to the Equation 2LiOH + Na₂CO₃ → Li₂CO₃+2NaOH, the profit about Li₂CO₃ is around $11.06. Meanwhile, the profit about H₂ harvest is around $0.014. The prices for the Na₂CO₃ ($4.25/kg) and Li₂CO₃ ($118.3/kg) were provided by [https://www.sinoreagent.com/](https://www.sinoreagent.com/). The price of H₂ ($5.5/kg) was obtained from the [https://prices.sci99.com](https://prices.sci99.com)

iv) The total operation time for our lithium recycling system to extract lithium resource from 1.0 kg spent LiFePO₄ batteries was about 20 h. The power of the motor was 0.12 kW. The electricity price in Beijing, China is $0.07/kW•h; therefore, the input cost of electricity for 1.0 kg of spent LiFePO₄ battery recycling was 20h × 0.12 kW × $0.07/kW•h = $0.168

Therefore, based on our lithium recycling system, the total profit for the lithium recycling from the 1 kg spent LiFePO₄ battery was $5.16.
Fig. S25 Cost assessment of the lithium recycling for the spent LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ battery based on the roll-to-roll system.
Fig. S26 Cost assessment of the lithium recycling for the spent LiCoO$_2$ battery based on the roll-to-roll system.
### Table S4 Comparison of different methods with respect to recycling lithium resources from spent batteries.

| Different methods        | Advantages                                                                 | Disadvantage                                                                                                                                                                                                 | References  |
|--------------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| Hydrometallurgy          | Possible to recycle lithium; room temperature operation                      | Low concentration of lithium (0.5-3 g/L) with high impurities in the solution after extraction of other metals; recycling efficiency is questionable; consumption of acid/alkaline solution | 12, 21, 22, 23 |
| Pyrometallurgy           | Easy to scale up; simple pretreatment; acid/alkaline-free                   | High energy consumption; emission of off-gas; lithium ends up in the slag (further treatment is needed)                                                                                                          | 18, 19      |
| Biometallurgy            | Less energy consumption                                                     | Bacteria are difficult to be cultivated; reaction kinetics is low; pulp density is low                                                                                                                              | 24          |
| Our work                 | Preserve electrode integrity; less energy consumption acid/alkaline-free; economic sustainable; applicable to various Li-containing cathodes |                                                                                                                                                                                                                |             |

**Movie S1.** All the possible movements for the lithium extraction of LiFePO₄ electrode based on our roll-to-roll recycle system. The lithium extraction system shows it can flexibly realize the forward rotation, rest, reverse rotation, rest and forward rotation actions.