RESEARCH ARTICLE

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Recovery of lithium salt from spent lithium-ion battery by less polar solvent wash and water extraction

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Abstract

The lithium hexafluorophosphate ($LiPF_6$) in spent lithium-ion batteries (LIBs) is a potentially valuable resource and a significant environmental pollutant. Unfortunately, most of the $LiPF_6$ in a spent LIB is difficult to extract because the electrolyte is strongly adsorbed by the cathode, anode, and separator. Storing extracted electrolyte is also challenging because it contains $LiPF_6$, which promotes the decomposition of the solvent. Here we show that electrolytes in spent LIBs can be collected by a less polar solvent dimethyl carbonate (DMC) wash, and $LiPF_6$ can be concentrated by simple aqueous extraction by lowering ethylene carbonate (EC) content in the recycled electrolyte. Due to the similar dielectric constant of EC and water, reducing the content of EC in LIB electrolytes, or even eliminating it, facilitates the separation of water and electrolyte, thus enabling the lithium salts in the electrolyte to be separated from the organic solvent. The lithium salt extracting efficiency achieved in this way can be as high as 99.8%, and fluorine and phosphorus of $LiPF_6$ can be fixed in the form of stable metal fluoride and phosphate by hydrothermal method. The same strategy can be used in industrial waste electrolyte recycling by diluting the waste with DMC and extracting the resulting solution with water. This work thus reveals a new route for waste electrolyte treatment and will also support the development of advanced EC-free electrolytes for high-performance, safe, and easily recyclable LIBs.

Hao Du, Yuqiong Kang, and Chenglei Li contributed equally to this study.

1 | INTRODUCTION

Lithium-ion batteries (LIBs) have become essential energy storage systems and are widely used in electronic devices, electric vehicles, and stationary energy storage.[1,2] However, because the operational life of modern commercial LIBs is only 5–10 years on average, large-scale use of LIBs will inevitably lead to the generation of substantial battery waste if not recycled. Globally, the mass of spent LIBs was estimated to be 4000 kilotons in 2022, and this figure is expected to eventually increase to over 100,00 kilotons.[3] Since spent LIBs contain about 45% metals and oxides, 38% polymers and carbon materials, 15% organic solvents, and 2% fluorine substances, disposing large quantities of spent LIBs would be a disaster in terms of environmental and resource sustainability.[4–11] Landfill of spent LIBs would lead to soil contamination by fluorine-containing substances and heavy metals, seriously damaging the natural ecological environment. Direct burn of spent LIBs is expected to increase by 1% greenhouse gas emission in the future. Therefore, it is important to develop reliable recycling procedures for spent LIBs.

State-of-the-art recycling strategies include pyrometallurgy, hydrometallurgy, and direct physical processes.[12–14] Unfortunately, these recycling processes are generally economic-oriented.[15] By pulverizing, separating, and element extraction, most high-value materials, such as cathode materials,[16–19] graphite, Cu foil, and Al foil, can be recycled. However, considerable low-value materials, including all fluorine-containing substances, especially electrolytes, are ignored.

The electrolyte is a major component of a LIB, accounting for about 12%–16% of its total mass. The mass of industrial electrolyte waste generated each year is comparable to the mass of spent LIBs.[4] Commercial electrolytes contain valuable lithium hexafluorophosphate (LiPF$_6$) and organic solvents; a typical LiPF$_6$ electrolyte may contain 0.84 mol/kg lithium salt and 5.04 mol/kg fluorine (Figure 1). Therefore, disposing of
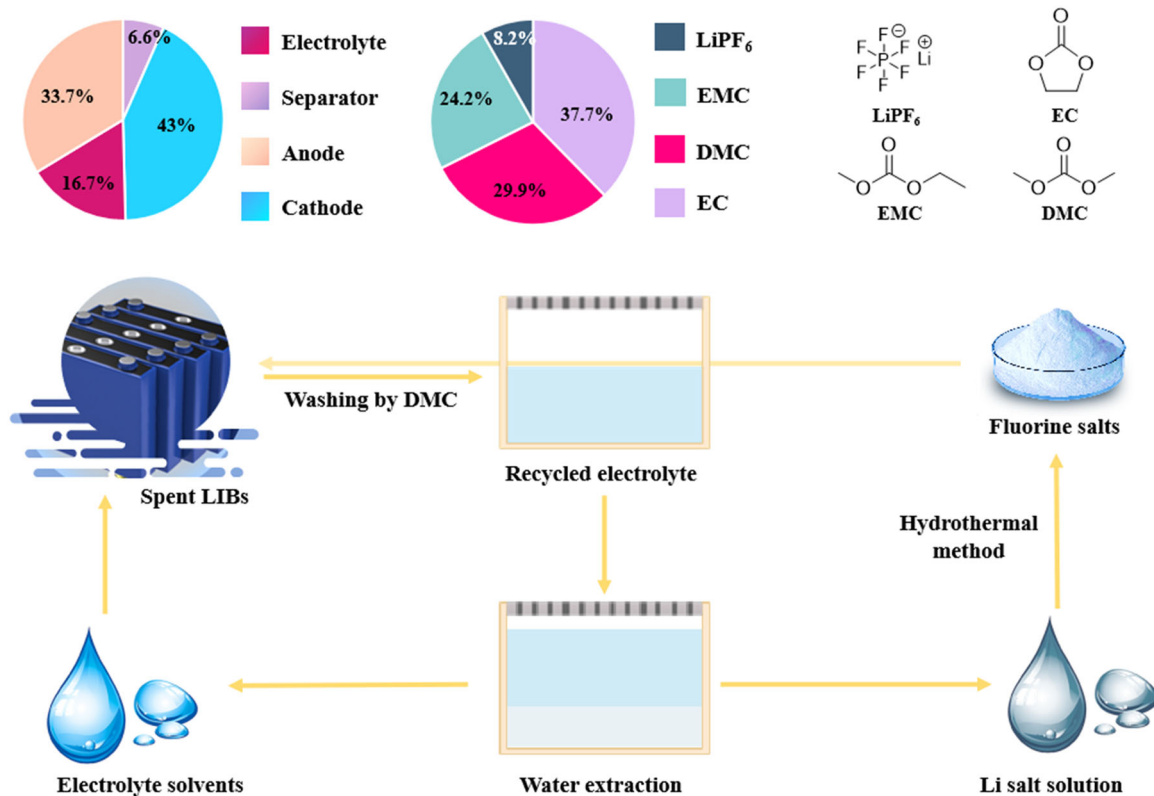

FIGURE 1 Schematic depiction of the waste electrolyte and its recycling process. Waste electrolyte from spent lithium-ion batteries (LIBs) is extracted and diluted with dimethyl carbonate (DMC) and then mixed with water to form a biphasic mixture, with the lithium salts being extracted into the aqueous layer for fluorine fixation. EC, ethylene carbonate; LiPF$_6$, lithium hexafluorophosphate.

the waste electrolytes by burning, as is commonly done now, wastes resources in addition to creating environmental problems.[20] Effective electrolyte treatment techniques are thus needed to improve the sustainability of the LIB industry.[21–23] Unfortunately, there are two issues with electrolyte recycling. The first one is that it is challenging to extract electrolytes from spent LIBs because much of the electrolyte in spent LIBs wets the electrodes and is strongly adsorbed. Also, the recycled electrolyte is sensitive to water and air, which causes the hydrolysis of LiPF$_6$ into PF$_5$, PF$_3$O, and HF.[24–26] These species can, in turn, induce the decomposition of carbonate solvents to form polyethylene glycol oligomers and other impurities, further degrading the electrolyte.[27] Electrolyte enrichment methods use mechanical, freezing, solvent extraction, or supercritical extraction.[21–23] Lithium salts in electrolytes have a high economic value compared to other components, so after enrichment, direct recovery or conversion methods are often used to obtain higher-value products by extracting or transforming the lithium salt.[28,29] Nevertheless, the extraction efficiency or purity of lithium salts obtained via these methods is often low, and reagents or machinery are often needed. Thus, green, safe, and high-recovery methods are necessary.

Here we show that electrolytes in spent LIBs can be collected by dimethyl carbonate (DMC) wash, and LiPF$_6$ can be concentrated by simple aqueous extraction by lowering ethylene carbonate (EC) content in the recycled electrolyte. Reducing the content of EC in LIB electrolytes, or even eliminating it, enables efficient aqueous extraction of lithium salts (Figure 1). We demonstrate that various lithium salts can be efficiently extracted from EC-free carbonate electrolytes. Then we show that reducing the EC content of existing commercial electrolytes by dilution with DMC permits efficient separation of LiPF$_6$ from organic solvents, and washing with DMC facilitates the extraction of LiPF$_6$ and organic solvents from spent commercial LIB cells. Finally, we outline strategies for isolating stable and unstable lithium salts from the aqueous extracts obtained using the above methods. One example of concentrated LiPF$_6$ solution treatment is presented for fluorine fixation.

2 | RESULT AND DISCUSSION

Ideally, extraction should be performed using a solvent (extractant) that is insoluble in the electrolyte but can efficiently extract lithium salts. The extractant's solubility depends on the electrolyte's dielectric constant. EC has a high dielectric constant (90) that exceeds that of water (81), whereas DMC and EMC have much lower dielectric

constants (3.1 and 2.9, respectively) (Supporting Information: Table S1). Therefore, reducing the electrolyte's content of EC should, in principle, facilitate the separation of water and electrolyte. The efficiency with which lithium salts in electrolytes can be separated from the electrolyte's organic solvent component depends mainly on the solvation-free energy of the salts in the electrolyte solvents and the extractant (H$_2$O) as well as the extraction-free energy. Figure 2 shows that the solvation-free energy of lithium salts in water is higher than that in DMC and EMC, but slightly lower in EC. Therefore, lithium salt readily interacts with H$_2$O and EC in a water/electrolyte mixture, as also evidenced by the favorable Gibbs free energy of Li$^+$ and PF$_6^-$ (Supporting Information: Table S2). Since EC in the electrolyte is diluted for the formation of a biphasic mixture, most lithium salt is extracted by water due to high solvation-free energy. Additionally, H$_2$O and EC have higher polarizability than DME and EMC, leading to a strong interaction with ions. Ab initio calculations show that the oxygen atom at the binding site between H$_2$O and EC and lithium ion has a stronger negative charge (−0.56 and −0.41 eV, respectively) than in DMC and EMC (−0.325 and −0.314 eV, respectively) (see Supporting Information: Figure S1). Moreover, simple mixing experiments show that pure EC is soluble in water, whereas DMC and EMC form separate layers when mixed with water (Figure 3a–c). Therefore, lithium salts should be much more readily extracted into the aqueous layer from EC-free or EC-less electrolytes.
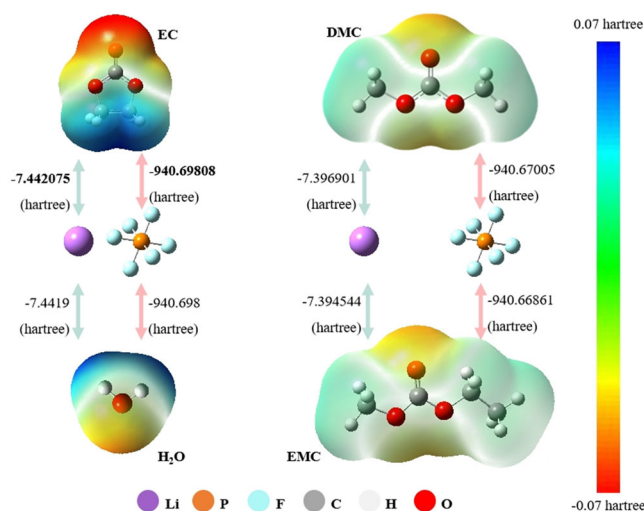

FIGURE 2 Theoretical analysis of water as an extractant for electrolyte separation. Solvation-free energy of Li$^+$ and PF$^-$ in electrolyte solvents and in the extractant (H$_2$O). DMC, dimethyl carbonate; EC, ethylene carbonate; LiPF$_6$, lithium hexafluorophosphate.
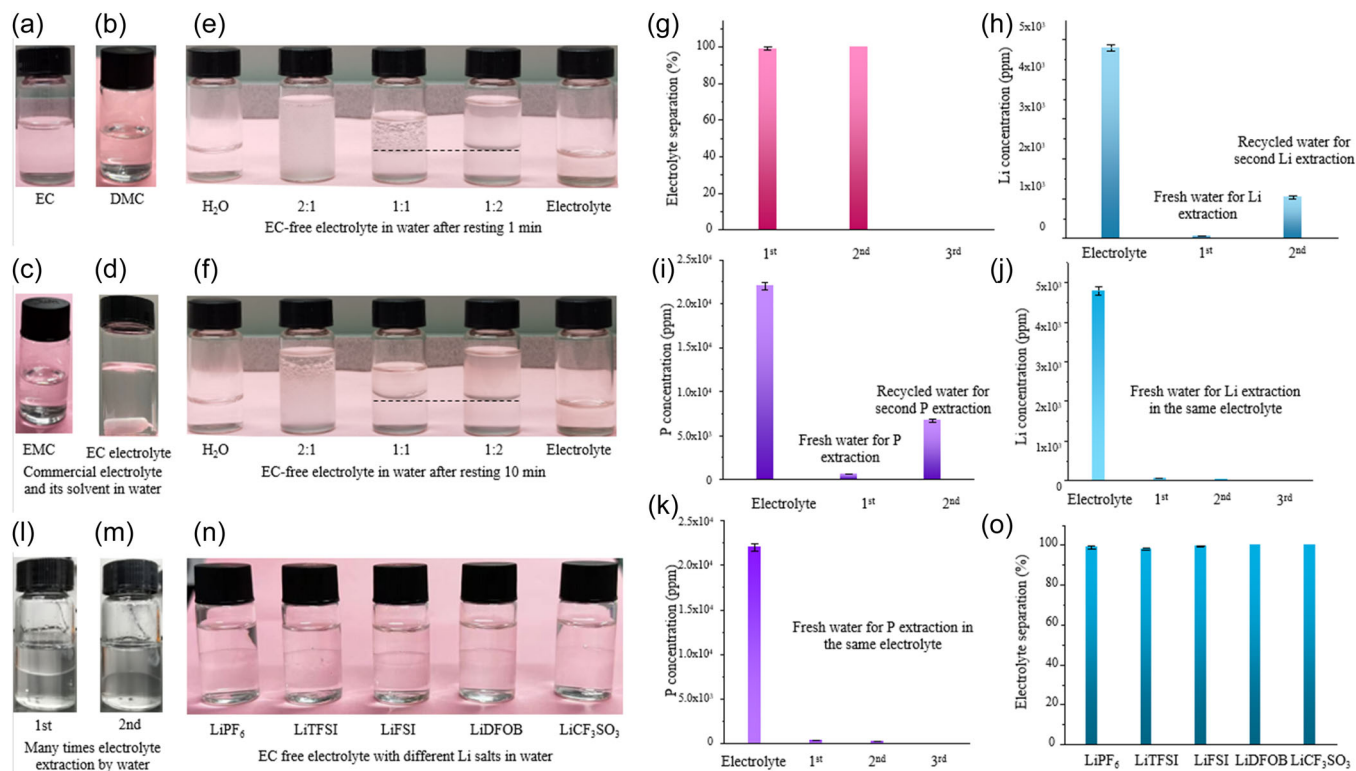
FIGURE 3 Separation of lithium salts from ethylene carbonate (EC)-free electrolyte samples using water. Optical images of mixtures of water and EC (a), dimethyl carbonate (DMC) (b), ethyl methyl carbonate (EMC) (c), and a commercial electrolyte (d). EC-free electrolyte (1 M lithium hexafluorophosphate [LiPF$_6$] in DMC and EMC) samples were mixed with different quantities of water after 1 min (e) and 10 min (f). Separation of EC-free electrolyte with water previously used to separate a different EC-free electrolyte sample (g). Lithium extraction efficiency from EC-free electrolyte with a reused aqueous solution (h). Phosphorus extraction efficiency from EC-free electrolyte using reused extraction water (i). Lithium extraction efficiency from EC-free electrolyte using fresh water (j). Phosphorus extraction efficiency from EC-free electrolyte using fresh water (k). First (l) and second (m) electrolyte extractions with fresh water. Optical images of EC-free electrolyte samples containing different lithium salts mixed with equal volumes of water (n) and the corresponding separation efficiencies (o).

Accordingly, when a commercial electrolyte consisting of 1 M LiPF$_6$ in an EC:DMC:EMC mixture (1:1:1 by volume) was mixed with an equal volume of water, the lower aqueous layer accounted for only around 10% of the total volume of the resulting biphasic mixture (Figure 3d). Conversely, when using an EC-free electrolyte (1 M LiPF$_6$ in DMC:EMC, 1:1 by volume), it was much easier to extract lithium salts by washing with 33%–50% water by volume (Figure 3e–f). It was also possible to extract two separate electrolyte samples sequentially using a single portion of water (50 vol%). However, in this case, the aqueous solution became more miscible with the electrolyte during the second extraction, possibly because of the high concentration of lithium salts in the water (Figure 3g). As a result, lithium and phosphorus extraction efficiencies were above 98% in the first extraction but only around 78% in the second (Figure 3h,i). The final concentration of LiPF$_6$ in the water after the second extraction was around 1.7 M. It was also possible to repeatedly extract the same electrolyte sample with different portions of fresh water; after performing three such extractions, the residual contents of lithium and phosphorus in the electrolyte were just 0.22 and 30 ppm, respectively, indicating extraction efficiencies above 99.8% (Figure 3j–m). The resulting electrolyte containing only trace quantities of lithium salts could be stored for extended periods under air at room temperature without appreciable degradation. Similar results were obtained in extraction experiments using EC-free electrolytes containing other lithium salts (Figure 3n,o). Overall, the results indicate that EC-free electrolytes containing different lithium salts can be efficiently separated using water.

We next investigated the effect of varying the electrolyte's EC content on the efficiency of electrolyte recycling. This revealed that reducing the EC content of electrolytes from 33 to 8.3 vol% by diluting it with DMC enabled a sharp increase in the extraction partition coefficient and efficient extraction of lithium salts with water (Figure 4a). The presence of EC reduced the
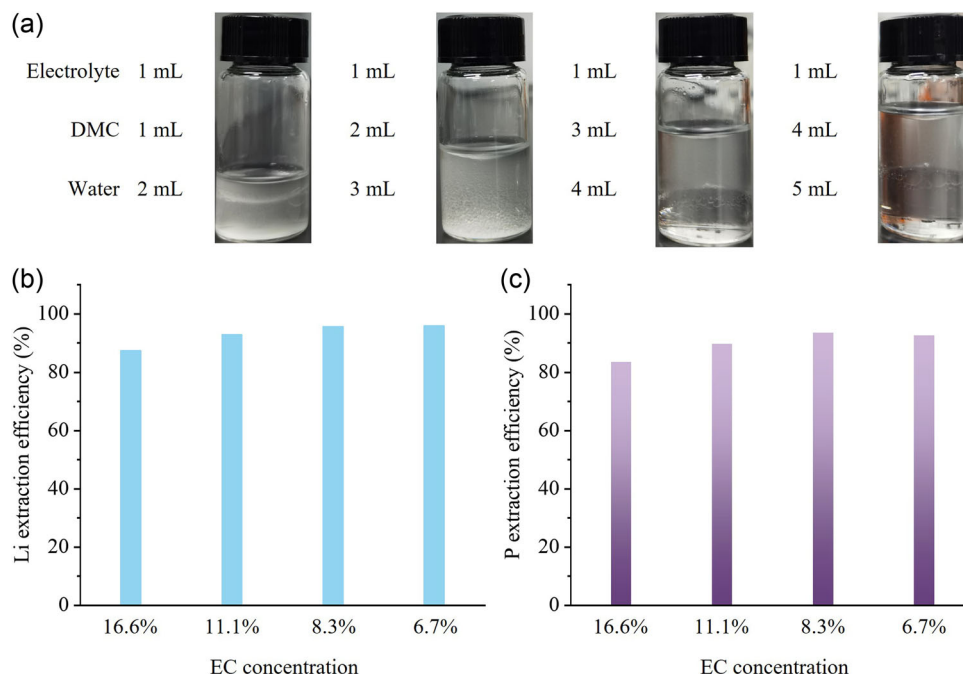
FIGURE 4 Separation of lithium salts from the organic solvent in a commercial electrolyte after dilution with dimethyl carbonate (DMC). (a) Optical image of the commercial electrolyte after dilution with different volumes of DMC and mixing with water. (b) Lithium extraction efficiency from the same commercial electrolyte after dilution with different volumes of DMC and water. (c) Phosphorus extraction efficiency from commercial electrolyte diluted with different amounts of DMC and then mixed with water. EC, ethylene carbonate.

overall extraction efficiency compared to that of EC-free electrolytes, but efficiencies above 95% for lithium and 92% for phosphorus were achieved nevertheless. Therefore, repeated washing with fresh water should enable near-complete separation of the lithium salts, even from electrolytes containing EC.

To demonstrate the applicability of the proposed method in the practical recycling of commercial LIBs, we disassembled two types of LIB cells from two manufacturers (Figure 5a–d). Our results revealed that the electrolyte distribution differed between different types of LIBs. Figure 5b shows no apparent liquid flow after opening the first cell, meaning that the electrolyte was wetting the cathode/separator/anode. The low boiling point liquids presumably evaporated quickly upon opening up the jellyroll cell, and there was no visible evidence of fluid on the electrodes. However, residual lithium salts and high boiling point solvents presumably remained adsorbed on the cathode/separator/anode. The second cell had a higher content of electrolytes, and around 150 g of electrolytes were poured out from the 3 kg cell after it was opened. This corresponds to approximately 25% of the total electrolyte mass in the cell (Figure 5d). After disassembling the cell, most of its electrolyte was wetting the jellyroll. Moreover, the electrolyte poured out was nontransparent and became

progressively darker when stored in the air, potentially indicating that it had become unsuitable for reuse (Figure 5e). This presumably happened because moisture in the air accelerates the decomposition of $LiPF_6$ into PF_5 and HF, which promotes the decomposition and polymerization of the carbonate solvent. This highlights the need for reliable ways to extract the electrolyte from spent LIB cells and separate the lithium salts.

There are two ways to extract the electrolyte from a jellyroll cell. One is to inject a liquid solution into the cell to wash the electrolyte out, as demonstrated by others. However, the internal structure of a jellyroll is very stable, and the cathode/separator/anode are difficult to separate because they are tightly pressed together by winding and hot pressing during cell assembly.[30] This is necessary to ensure stable battery performance and avoid hazardously uneven lithium deposition. Consequently, it is challenging to completely extract the electrolyte by the direct injection method. To demonstrate this, we discharged a $LiFePO_4$ cell to 3.2 V (Li/Li$^+$), meaning that the anode retained a small quantity of active lithium. Upon opening this cell and soaking it in water (Figure 5f), a large amount of water entered the cell's interior, forming hydrogen bubbles as water molecules reached the anode and reacted with its residual active lithium. However, bubbling continued for at least 2 days,
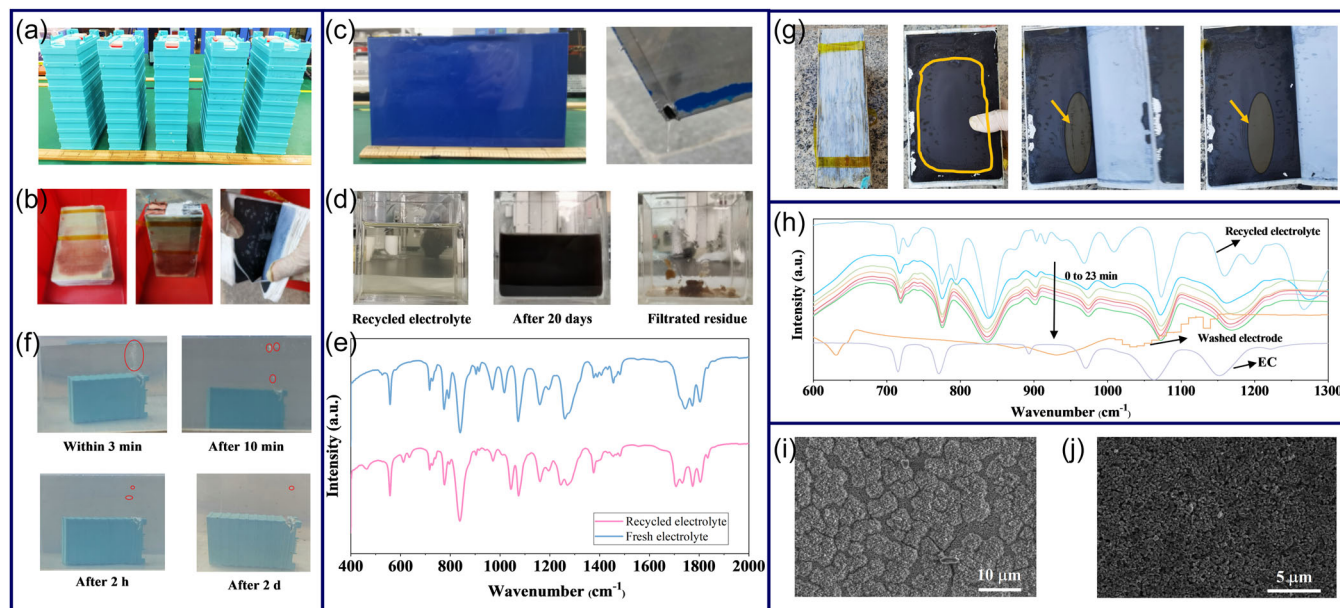
FIGURE 5 Disassembly of commercial lithium-ion battery (LIB) cells and electrolyte recovery. (a) Picture of a commercial LIB cell. (b) Picture of the commercial LIB cell after shell removal. (c) Picture of a commercial LIB cell from another manufacturer. (d) Picture of recycled electrolyte in air. (e) Fourier-transform infrared (FTIR) spectrum of recycled electrolyte. (f) Picture of opened commercial LIB cell in water. (g) Picture of the disassembled electrode. (h) FTIR spectrum of the disassembled electrode. (i) Scanning electron microscope (SEM) image of the disassembled electrode after 1 month in air. (j) SEM image of the disassembled electrode after washing with water and storage for 1 month in air. DMC, dimethyl carbonate; EC, ethylene carbonate; EMC, ethyl methyl carbonate; LiPF$_6$, lithium hexafluorophosphate.

demonstrating the difficulty of fully extracting the electrolyte from a partially disassembled cell using aqueous solutions. Indeed, when the cell shell was completely removed after 2 days, it became clear that only half of the electrode surface area had been wetted by the aqueous solution, demonstrating the slowness of the electrolyte extraction process. In addition, low boiling point solvents were still present in the electrode and evaporated rapidly upon exposure to the air (Figure 5g). This further demonstrates the difficulties of direct electrolyte extraction from cells using aqueous solutions.

The second method requires the direct removal of the cell shell and opening of the jellyroll structure. Upon opening and unrolling the jellyroll structure, the low boiling point solvents (DMC and EMC) evaporated, but the high boiling point EC and lithium salts remained on the electrode. The original electrolyte's Fourier transform infrared spectrum has strong peaks at 800, 1020, 1200, and 1270 cm^{-1} (Figure 5h). After opening the cell and removing the electrode, the intensity of these peaks declined rapidly; they were completely absent after 4 min, and the remaining peaks coincided almost perfectly with those of EC. Because LiPF$_6$ is a solid inorganic salt, it was deposited on the electrode surface with the EC; these residues ultimately formed a white substance that coated the electrode surface after a week or so (Figure 5i).

Based on these results, we recommend disassembling cells and recovering the electrolyte by washing them with DMC. Although this process will inevitably lose some of the volatile electrolytes, exposure to the resulting odor can be minimized by performing the cell disassembly process in a fume hood. After disassembly, the electrolyte's organic solvent and lithium salt components can be collected by soaking the isolated cathode and separator in DMC. Figure 5h shows that subsequent washing with DMC completely removed 94% residual organic electrolyte from these components, leaving a clean electrode surface and a DMC electrolyte solution that could be extracted with water to separate the lithium salts. Inductively coupled plasma results show trace amounts of Fe, Ni, and Cu impurities in the extracted aqueous solution. The purity of lithium exceeds 99.9% (Supporting Information: Table S6).

The treatment of the aqueous extracts obtained using the above procedure depends on the types of lithium salts present. The stable lithium salts, such as LiTFSI and LiSO$_3$CF$_3$, can be purified and reused in LIBs. LiPF$_6$ is sensitive to water and is degraded to release PF$_5$, which then reacts with water to form hydrofluoric acid (Figure 6a). This makes it difficult to separate LiPF$_6$ directly. Although HF can be neutralized with bases such as LiOH to obtain fluoride salts, LiPF$_6$ is difficult to be fully decomposed due to the high dissociation energy.
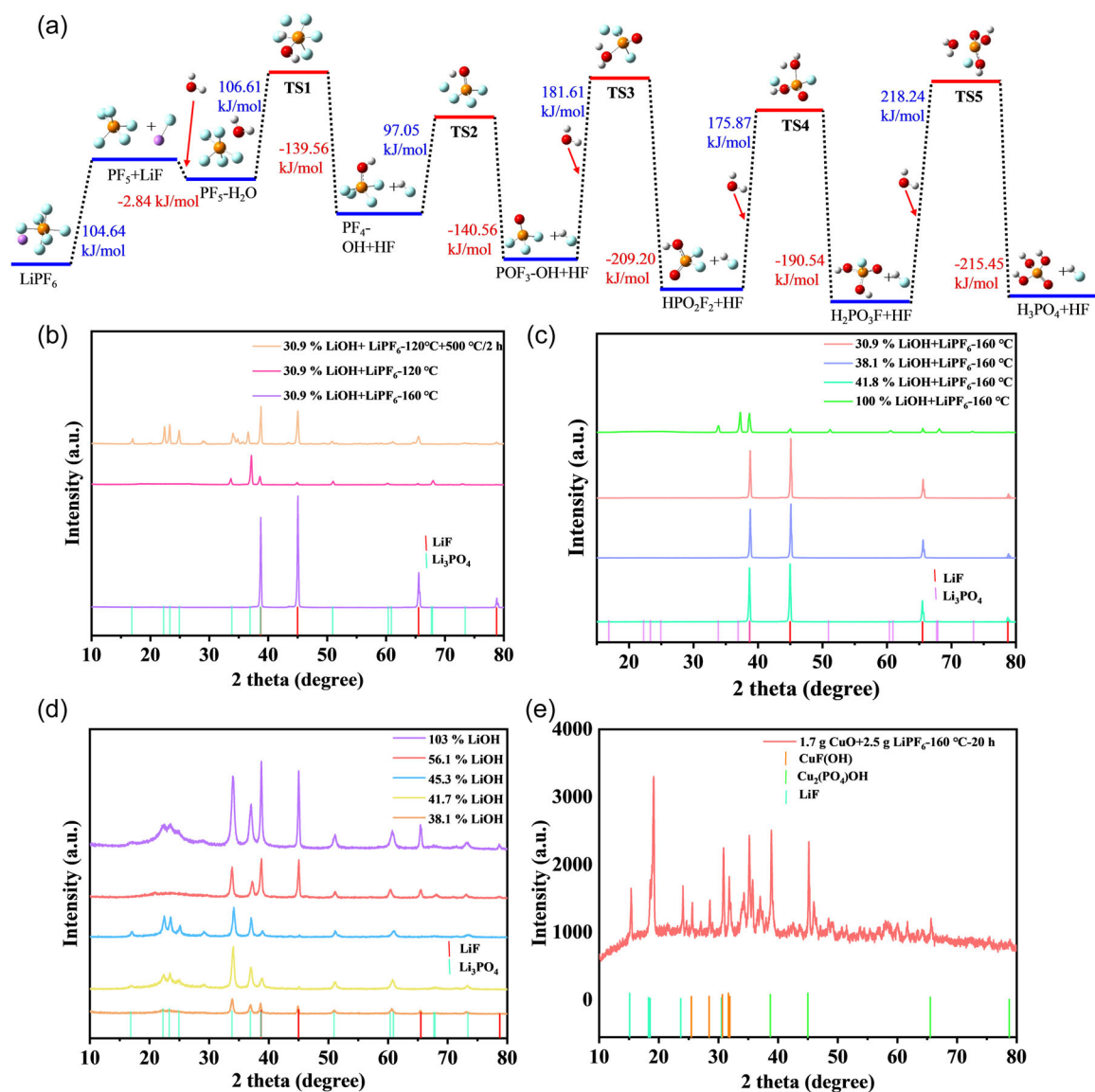
FIGURE 6 Aqueous lithium hexafluorophosphate ($LiPF_6$) solution conversion. The theoretical ratio of $LIPF_6$ reacting with $LiOH \cdot H_2O$ is 8 M $LiOH \cdot H_2O$ when adding 1 M $LiPF_6$ to generate 6 M LiF and 1 M Li_3PO_4. (a) Density functional theory (DFT) calculation of $LiPF_6$ hydrolysis process. (b) $LiPF_6$ conversion at different temperatures. (c) $LiPF_6$ conversion with different content of $LiOH \cdot H_2O$ at 160°C. (d) Precipitation of $LiPF_6$ hydrolysis solution with the addition of $LiOH \cdot H_2O$. (e) $LiPF_6$ conversion with CuO.

The hydrolysis of $LiPF_6$ includes 12 elementary steps (Supporting Information: Table S3), and most dissociation energies are much higher than 100 kJ/mol, demonstrating that hydrolysis of $LiPF_6$ needs harsh conditions (Figure 6a).

The hydrothermal method can be used for efficient $LiPF_6$ conversion. Under room temperature and 80°C, 20 mL 30.9% $LiOH \cdot H_2O$ (2.47 M) and 1 M $LiPF_6$ aqueous solution obtain no precipitation after 20 h, demonstrating limited hydrolysis of $LiPF_6$. Further increasing the temperature to 120°C enables the generation of approximately 0.7 g white powder, an unknown crystal substance. This crystal can be converted to LiF and Li_3PO_4

after 500°C thermal treatment for 2 h. Increasing the temperature to 160°C yields 1.2 g (38%) of pure LiF solids (Figure 6b). With the optimized condition of 160°C and 20 h, we increase the content of $LiOH \cdot H_2O$ from 30.9%, 38.2% to 41.8%, all of which can achieve pure LiF powder. One hundred percent $LiOH \cdot H_2O$ can produce a mixture of LiF and Li_3PO_4, of which the yield of lithium fluoride is about 80% (Figure 6c). Moreover, we investigated the reacted 30.9% $LiOH \cdot H_2O$ (2.47 M) and 1 M $LiPF_6$ solution for further precipitation. We took 10 mL solution and added $LiOH \cdot H_2O$ multiple times. When adding 3.6% $LiOH \cdot H_2O$ three times, all the precipitated powder was LiF except a small amount of

Li_3PO_4. The fourth addition of $LiOH \cdot H_2O$ was almost no precipitation of Li_3PO_4, while a large amount of precipitation of LiF and Li_3PO_4 was generated during the fifth addition. Adding $LiOH \cdot H_2O$ no longer causes turbidity after the solution becomes weak alkalinity (Figure 6d). Therefore, it can be proved that the HF and H_3PO_4 in the solution can be completely precipitated.

In addition, we also demonstrated that other chemicals can also fix the fluorine and phosphorus of recycled $LiPF_6$. As shown in Figure 6e, 1.7 g CuO and 2.5 g $LiPF_6$ for hydrothermal reaction can obtain a mixture of $Cu_2(PO_4)F$, $Cu_2PO_4(OH)$, and LiF.

Profitability is a crucial aspect to consider for the feasibility of electrolyte recycling. We measured the economic analysis of electrolyte recycling based on an electrolyte system comprising 84.1% carbonate solvents, 7.7% lithium salt $LiPF_6$, and 9.2% additives. The price of each material and the profit gained from recycling one ton of electrolyte are shown in Tables S4 and S5, respectively. The results show that the cost of electrolyte recycling is mainly associated with the consumption of LiOH, which amounts to ¥33,069/kg electrolyte and represents about 89.0% of the total cost. The revenue of ¥36,313/kg electrolyte from LiF is comparable to the recycling cost of ¥37,168/t electrolyte. Revenue from Li_3PO_4 is also considerable about ¥19,391/t electrolyte. Therefore, recycling electrolyte is profitable even for fluorine and phosphorus extraction. Moreover, if the carbonate solvent can be regenerated, the theoretical profitability would increase substantially to ¥24,416/t electrolyte.

3 | CONCLUSION

This work presents a novel strategy for separating and recycling the components of electrolytes used in LIBs. It was demonstrated that the separation of lithium salts and organic solvents are facilitated by using electrolytes that are free of EC or by diluting EC-containing electrolytes with less polar carbonate solvents such as DMC. This is because, unlike EC, these solvents have much lower dielectric constants than water. Consequently, the solvation-free energy of lithium salts in these solvents differs substantially from that in water, so the lithium salts tend to distribute into the aqueous layer when EC-free electrolytes are extracted with water, providing aqueous solutions with high lithium salt concentrations. Separating lithium salts from electrolyte solvents in this way could alleviate problems caused by the need to store large quantities of industrial electrolyte waste and enable the profitable recovery of lithium salts. A similar strategy involving washing disassembled LIBs with DMC and

extracting lithium salts from the resulting DMC solutions can extract and concentrate lithium salts from spent LIBs. The $LiPF_6$ concentrated aqueous can be treated for fluorine fixation by hydrothermal treatment. Additionally, previous reports have demonstrated EC-free electrolytes exhibiting intrinsic safety and superior high-voltage stability.[31,32] These results suggest that developing EC-free electrolytes would facilitate the creation of LIBs that are more easily recyclable than those used today while still being safe and offering a good performance.[33]

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SUPPORTING INFORMATION

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