

RESEARCH ARTICLE

Cathode Recycling of Spent Sodium Ion Batteries

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Sodium-ion batteries (SIBs) have been commercialized in 2023 and are expected to capture a substantial market share in the future. However, the material systems in SIBs are very similar to those in lithium-ion batteries (LIBs), which necessitate consideration of recycling in terms of safety issues, environmental concerns, and economic values. In this study, we present the first evaluations of the disassembly of spent commercialized SIBs and the leaching and regeneration of their cathode material ($\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$). We find that pretreatment of SIBs recycling offers advantages, particularly in separating the cathode and removing impurities from the material surface. The primary challenge in recycling is that failed cathode materials are difficult to dissolve in traditional inorganic acids, with an extraction rate of only 57.4% even when a reducing agent is added. Fortunately, there is a possibility for the failed $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ regeneration. By replenishing sodium and repairing the structure through thermal treatment, the capacity can be restored to 109.4 mAh g^{-1} , with potential practical applications. Economic analysis indicates that the recycling of spent SIBs through cathode material regeneration results in a profit of $\$3.76 \text{ kg}^{-1}$ battery, even surpassing the $\$2.64 \text{ kg}^{-1}$ battery profit from LIB recycling. We hope that this research will provide a foundation for SIB recycling.

Introduction

The severe issues of energy shortages and environmental pollution make the research and development of renewable energy storage and utilization more urgent. However, most renewable energy sources have intermittent and unstable outputs, limiting their practical application [1–3]. To improve the efficiency of renewable energy use, electrochemical secondary batteries have emerged as an ideal solution due to their efficiency, portability, and safety [4–7]. Lithium-ion batteries (LIBs), in particular, are one of the most commercially successful and widely used technologies because of their long cycle life, low self-discharge, high operating voltage, and high energy and power densities [8–10]. Nevertheless, the cathode materials of LIBs contain elements like lithium, cobalt, and nickel, which are unevenly distributed and relatively scarce in the Earth's crust [11,12]. This rarity leads to instability of the LIB industry. This has resulted in the exploration of other low-cost and high-performance battery systems. The sodium-ion batteries (SIBs) industry has seen significant development in recent years [3,7,13,14]. The imbalance between lithium resource supply and demand has led to the significant fluctuation of lithium prices, further promoting the development of SIBs [11,12]. Although SIBs have a lower energy density compared to LIBs, they offer high safety, a wide operating temperature range, good rate performance, and low costs. These advantages position SIBs to play a crucial role in energy storage and low-speed electric vehicle applications in the future [15,16].

With the commercialization of SIBs and their immediate utilization in energy storage system in 2023, it is projected that their market share will steadily increase, with an annual demand potentially reaching 500 GWh in 2030 [17]. However, SIBs share a similar structure and material system to LIBs, raising significant safety and environmental concerns regarding their disposal [18]. For instance, SIBs contain 13 wt.% flammable materials, 26 wt.% carbon materials, and 1.4 mol kg^{-1} batteries fluorine [17]. If spent SIBs are disposed of improperly by landfilling or burning, they can cause severe fire hazards and carbon emissions, and pose significant health risks. Therefore, during the early stages of SIB commercialization, exploring recycling strategies is essential. This effort can guide the optimization of future SIB material systems, minimize their environmental impact throughout their lifecycle, and promote the sustainable and healthy development of the industry.

This paper presents an investigation on recycling commercial $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NFM)-based 18,650 cylindrical cells. We selected NFM batteries because their system is highly similar to the current $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ batteries, which helps in understanding the difficulties of recycling SIBs compared to LIBs. We conducted a comprehensive failure analysis of SIBs, from the battery level down to the material level, and examined the processes of battery disassembly, cathode separation, material element extraction, and regeneration. Our findings indicate that the pretreatment of spent SIBs is comparatively easier than that of LIBs, particularly in terms of electrode separation and the removal of material interface impurities. Although leaching

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the NFM material after failure is challenging, material regeneration seems to be simpler.

Materials and Methods

Materials

Cylindrical SIBs (1.5 Ah) are provided by Jiangsu Chuanyi Sodium Battery Technology Co., Ltd. The battery-grade sodium metal foils, super-conductive carbon black (SP), polyvinylidene fluoride (PVDF binder), and dimethyl carbonate are purchased from Guangdong Canrd New Energy Technology Co., Ltd. *N*-Methyl-2-pyrrolidone (NMP) and anhydrous sodium carbonate are purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Additionally, 1.0 M NaClO₄ in ethylene carbonate (EC):diethyl carbonate (DEC) 1:1 vol.% with 5% fluoroethylene carbonate (FEC) is purchased from Suzhou Duo Duo Chemical Technology Co., Ltd.

Battery disassembly

The 1.5-Ah batteries are cycled until the battery capacity reduces to below 80% of the theoretical capacity. At this point, the battery is considered to have reached the end-of-life criteria. Before dismantling the batteries, they are discharged at a rate of 0.1 C to 0.1 V. Both end-of-life and new cylindrical batteries are dismantled and separated within a glovebox (with water and oxygen levels below 0.1 parts per million) to prevent moisture and oxygen from affecting the materials. The specific procedure involves removing external terminals and aluminum-plastic films, exposing the jellyroll. The separated cathode (denoted D-NFM), separator, and anode are individually stored.

Electrode separation

The separated electrodes are cut into 3 cm × 3 cm pieces. In a 50-ml beaker, 10 ml of deionized water is added to these cut electrode pieces and left to stand for 10 s. At this point, the active materials have separated from the current collector. The separated active materials are placed in an oven for 12 h at 80 °C.

Cathode leaching

The leaching solution is prepared using 1 mol l⁻¹ sulfuric acid as the leaching acid and 5 vol.% H₂O₂ as the reducing agent. Separated active materials and the prepared leaching solution are added according to a solid-liquid ratio of 50 g l⁻¹. The leaching process is conducted at 20, 40, or 60 °C for 1 h, as well as at 20 °C for 30 s, 1 h, 6 h, 12 h, and 24 h. The leaching efficiency is calculated based on the inductively coupled plasma (ICP) test results.

Cathode regeneration

The water washed D-NFM (D-NFM-W) is mixed with anhydrous sodium carbonate at molar ratios of 65%, 70%, and 75%. The mixture powder is ground under infrared light for 10 min and then thermal treated in a muffle furnace at a ramp rate of 5 °C min⁻¹ to 900 °C for 10 h. The regenerated cathode is named S-65%, S-70%, and S-75% based on sodium carbonate addition.

Electrochemical test

The regenerated materials are mixed with PVDF and conductive carbon black in NMP at a mass ratio of 8:1:1. The slurry is then coated onto aluminum foil and vacuum-dried at 120 °C for 12 h. Coin cells are assembled in a glovebox under argon

atmosphere, using sodium metal with a diameter of 15.6 mm as the anode and the 14-mm cathode as the cathode. The cells are assembled with 1.0 M NaClO₄ in EC:DEC 1:1 vol.% electrolyte with 5 vol.% FEC additive, using GF/A fiber glass as the separator. Cycling performance tests are conducted in the voltage range of 1.5 to 4.0 V under different current densities. Electrochemical impedance spectroscopy and cyclic voltammetry are performed using an electrochemical workstation.

Characterization

X-ray diffraction (XRD) spectroscopy is employed to characterize the crystal structures of the cathode and anode materials using a D8 Advance Bruker instrument under 45 kV, 40 mA, and a scan rate of 10° min⁻¹. X-ray photoelectron spectroscopy (XPS) is used to analyze the elemental valence on the cathode surface with a VersaProbeII ULVCA-PHI instrument. For the XPS analysis, a monochromatic Al K α X-ray source is used, with settings of 100 μ m, 25 W, and 15 kV, and depth analysis is performed using Ar ion sputtering at 2 kV. Field emission scanning electron microscopy (SEM, SU-8010 Hitachi) and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F30 FEI) equipped with an aberration-corrected high-angle annular dark-field detector are used to characterize the material morphology and structure. ICP optical emission spectrometry is employed to determine the elemental content in the cathode and anode materials using an Arcos II MV SPECTRO instrument. X-ray computed tomography (CT) is used for nondestructive detection of internal structural changes in the battery with a nanoVoxel-4000 system.

Results and Discussion

Battery disassembly

We conducted computed tomography on both spent cylindrical SIBs (cathode denoted as D-NFM) and pristine ones (cathode denoted as NFM) to observe internal changes. As depicted in Fig. 1A, the spent battery maintains a well-defined cylindrical structure, with the winding of electrodes still clearly visible from the top view, indicating that the electrode integrity remains intact even after extended cycling. Hence, it is suitable for SIBs to be recycled by disassembling method. The disassembled electrode surface after cleaning with DMC (Dimethyl carbonate) appears smooth for NFM, whereas white spots are evident on D-NFM, primarily due to the formation of a cathode electrolyte interface (CEI) layer on the cathode after prolonged cycling, comprising mainly sodium salts and organic compounds (Fig. 1A). This also demonstrates that DMC is insufficient in completely removing impurities at the material interface. Moreover, the presence of more obvious white spots on degraded hard carbon (D-HC), as observed through HC and D-HC, correlates with the storage mechanism of sodium ions in hard carbon [19–21].

We subsequently investigated the electrode separation. Separating the cathode under conventional conditions is challenging owing to the use of PVDF as a binder. We found that using water as the separation medium effectively induced the delamination of the cathode materials from the aluminum foil. This likely occurs because the layered cathode material in SIBs is relatively unstable in air and readily reacts with moisture to trigger sodium ion loss, forming NaOH. In aqueous solution, it is easier for H⁺ in water to replace sodium ions in the layered material, producing NaOH (Fig. 1B). This NaOH reacts with the aluminum, forming AlO₂⁻, and causes the active material to

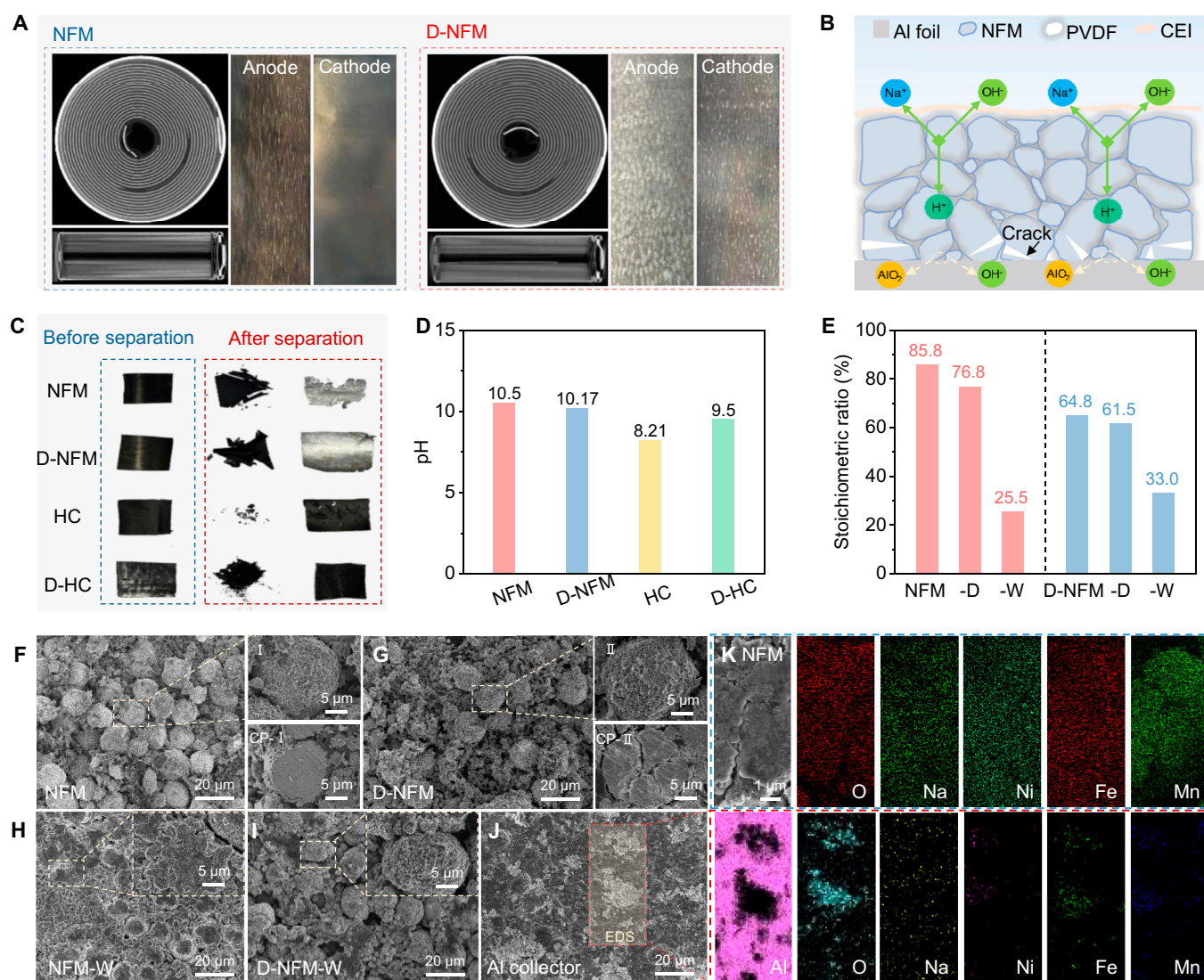


Fig. 1. (A) CT images of NFM and D-NFM cells and optical images of corresponding disassembled electrodes. (B) Schematic illustration of cathode separation in water. (C) Results of electrode separation. (D) pH values of electrode immersion in water. (E) Sodium ion ratio in materials before and after immersing in water. (F) SEM images of pristine NFM. (G) SEM images of D-NFM. (H) SEM images of NFM after immersing in water (D-NFM-W). (I) SEM images of D-NFM after immersing in water (D-NFM-W). (J) SEM images of recycled current collector. (K) EDS images of NFM and recycled current collector. In these abbreviations, "D" represents degraded, and "W" represents water leaching.

separate from the current collector [22,23]. This reaction is rapid, achieving complete separation of the active material from the current collector within 10 s. Figure 1C illustrates the separation results, showing that the aluminum current collector from D-NFM is more intact compared to NFM. This is because D-NFM has a lower sodium ion content of about 80%, resulting in less NaOH and a milder alkaline reaction with aluminum, thus preserving the integrity of the separated current collector (Fig. 1D). Conversely, water as a separation medium is less effective for anode materials (HC and D-HC). This inefficacy can be attributed to the lower sodium ion content in the anode, leading to a less alkaline solution compared to that of the cathode material.

To confirm that the observed separation is due to NaOH in the solution, we measured the sodium ion content and pH of the solution. Under identical conditions, we immersed NFM, D-NFM, HC, and D-HC in water, resulting in alkaline solutions with pH values of 10.5, 10.17, 8.21, and 9.5, respectively, which

corresponds with the separation trends of cathode materials from the current collector (Fig. 1D). ICP analysis confirmed a significant reduction in sodium ion content in the materials after water treatment, demonstrating that sodium ions leached from the materials into the solution (Fig. 1E).

The cathode separation not only extracts sodium ions from the cathode but also removes surface impurities. The surface of the failed NFM is covered with a thick CEI layer (Fig. 1F and G), primarily composed of NaF, Na_2CO_3 , Na_2O , and organic species, all of which are highly water-soluble. Consequently, washing the NFM with water leads to noticeable surface changes. After D-NFM is thoroughly washed with a large amount of water, the surface shows distinct primary particles, closely resembling the original material (Fig. 1H).

Further analyses on the current collectors indicate that the aluminum foil surface exhibits some residual active materials (Fig. 1I). SEM image shows that when the cathode is immersed in water, part of the cathode material fractures, some remain

on the current collector's surface, and some detach completely from the current collector, also facilitating cathode separation. ICP analysis confirms the elemental composition of these residues: sodium at 1.34 mol%, nickel at 1.96 mol%, iron at 2.41 mol%, and manganese at 1.94 mol%. Using water as a separation medium proved to be a simple and efficient method for separating cathode materials from aluminum foil.

Materials analysis

Surface analysis

The CEI compositions are the main impurity sources introduced into the material during the recycling process. Therefore, tracking changes in surface impurities during recycling is crucial for the final quality of the recovered material. We use 3D tomography of TOF-SIMS to examine the surface changes of cathode materials. As shown in Fig. 2A, the D-NFM surface contains abundant fluorine and phosphorus, largely due to NaPF_6 -induced CEI formation. When the cathode is washed 3 times with DMC, the concentrations of fluorine and phosphorus are significantly reduced and almost negligible after a depth of 100 nm (Fig. 2B). When the cathode is quickly rinsed 3 times with water, the fluorine and phosphorus nearly disappear, showing very low detectable intensities (Fig. 2C). This indicates that water not only separates the active materials from the current collectors but also effectively removes the surface CEI.

XPS depth profiles of D-NFM before and after water washing further indicate that water effectively removes CEI from

the cathode material, with detectable fluorine levels below 1% (Fig. 2D). Although the phosphorus signal in D-NFM-W occasionally fluctuates near zero and even shows negative values at times, it is similar to the NFM-W signal, indicating negligible phosphorus content in the material. Considering that the CEI's proportion in the cathode material is very limited, the impurities remaining after washing are insignificant and do not affect the quality of the recovered material (Fig. 2E).

Beside the CEI, NFM interphase is also changed after extensive cycling. The XPS results shown in Fig. 2F indicate that the valence state of nickel changes from +2 to +3 [24,25]. In the NFM system, nickel undergoes redox reactions during charging and discharging up to 4.0 V [26], while iron and manganese mainly stabilize the transition metal layers [27,28]. The oxidation of some nickel in D-NFM compensates for the loss of sodium ions, achieving charge balance by increasing nickel's valence state [26]. NFM with interface changes, especially where an increase in the valence state of material elements necessitates the assistance of reducing agents for dissolution. The XPS spectra of NFM, D-NFM, and D-NFM-W showed that the oxidation state of Fe is +3 and that of Mn is +4 (Figs. S1 and S2). This indicates that during the charge and discharge processes, Fe and Mn ions do not participate in redox reactions, helping to maintain the lattice structure. After separation using water as the medium, the oxidation states of Fe and Mn ions remain unchanged, suggesting that charge compensation during the separation process is achieved by Ni ions.

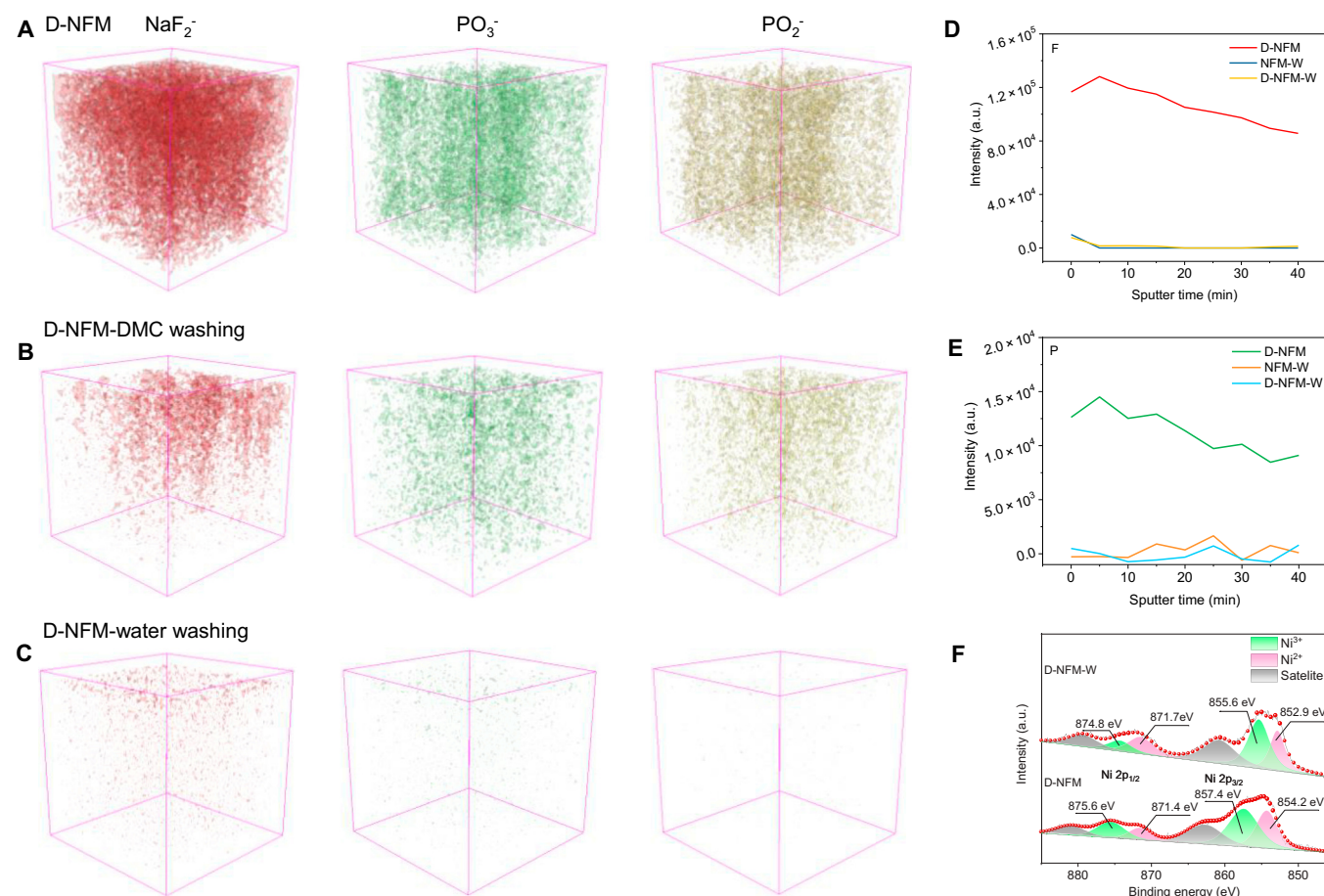


Fig. 2. TOF-SIMS 3D tomography of D-NFM (A), D-NFM-DMC (B), and D-NFM-W (C). (D) XPS depth profile of F in D-NFM and D-NFM-W. (E) XPS depth profile of P in D-NFM and D-NFM-W. (F) XPS profile of Ni in D-NFM and D-NFM-W.

Structure analysis

The structural changes in NFM are crucial for material leaching or regeneration, significantly impacting how materials dissolve or undergo repair. After cycling, the material exhibits numerous cracks within its particles (Fig. 1F and G). While these changes facilitate material dissolution due to increased surface area, they pose challenges for material regeneration. Internal CEI formation and the need for high-temperature sintering to address cracks may further complicate restoration efforts.

XRD is used to determine the changes in the materials' microstructure. The NFM exhibits clear characteristic peaks at (003), (102), and (104) (Fig. 3A and Table S1) [26,27]. This confirms that NFM has an O3 phase structure, and the high intensity ratio between (104) and (102) indicates a well-defined layered structure [29]. In contrast, the D-NFM material shows distinct peaks at (003), (012), and (015) (Fig. 3B and Table S2). The refined results reveal a composite phase of P3 and O3, with the P3 phase comprising 76.4% of the material. Additionally, the intensity ratio between (015) and (012) is significantly lower

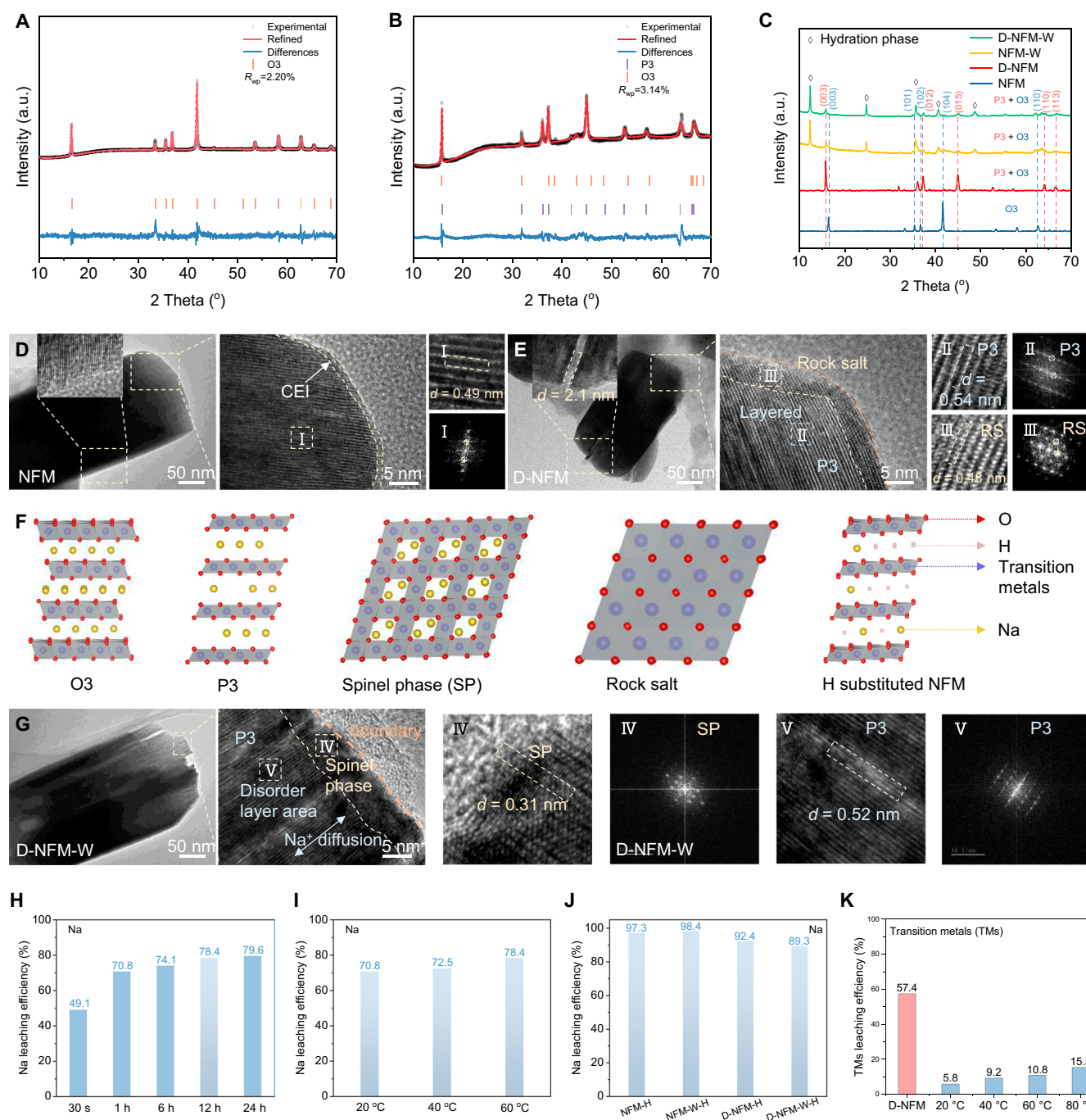


Fig. 3. The Rietveld refinement of the XRD pattern for (A) NFM and (B) D-NFM. (C) XRD patterns of NFM and D-NFM before and after water immersion. (D) TEM images of pristine NFM. (E) TEM images of D-NFM showing P3 and rock-salt phases. (F) Schematic illustration of different phases presented in this study. (G) TEM images of D-NFM-W showing P3 and spinel phases. (H) Sodium leaching efficiency of D-NFM in water for various times. (I) Sodium leaching efficiency of D-NFM in water at various temperatures. (J) Sodium leaching efficiency in 5% H₂O₂ 1 M H₂SO₄ solution. (K) Transition metal leaching efficiency in 5% H₂O₂ 1 M H₂SO₄ solution.

compared to NFM, suggesting that prolonged cycling causes transition metal migration, weakening the layered structure. Moreover, the (003) peak of D-NFM shifts slightly to the left because of the loss of active sodium ions within the layered structure [24,30]. This increases the repulsive forces between the transition metal layers, enlarging the interlayer spacing. The XRD results of the materials after water immersion separation are shown in Fig. 3C. For NFM-W and D-NFM-W, distinctive peaks of hydrated phases appear due to the reaction between H^+ in water and sodium ions in the layered structure [31–34]. Peaks such as (003) and (012) of the P3 phase are still present but with reduced intensity, indicating that the layered structure is retained after immersion.

To further investigate the structural changes in the cathode material, we performed TEM characterization. To showcase the material failure, we present schematic diagrams of different phases in Fig. 3F. The TEM results clearly reveal the (003) crystal planes of both NFM and D-NFM, with interplanar spacings of 0.49 nm (Fig. 3D, region I) and 0.54 nm (Fig. 3E, region II), respectively. The lattice diffraction patterns indicate that NFM exhibits an O3 phase (Fig. 3D) [24,27], while D-NFM displays a P3 phase (Fig. 3E), consistent with the XRD results. For D-NFM, we find the disappearance of the CEI layer on the particle surface, which corroborates the TOF-SIMS results shown in Fig. 2C. Additionally, a near 10-nm rock-salt phase layer is visible on the surface of the D-NFM material, particularly in region III of Fig. 3E. This formation is due to excessive sodium ion depletion, which facilitates the migration of transition metals to sodium ion sites, forming a rock-salt phase that significantly hinders sodium ion intercalation and deintercalation.

Figure 3G displays TEM images of the water-treated cathode materials. Numerous cracks are observed along the sodium ion transport pathways, likely caused by the rapid extraction of sodium ions. Additionally, comparing the TEM results of D-NFM reveals a transformation of the impurity phase from a rock-salt structure to a spinel structure at the material interface after water treatment (Fig. 3G, regions IV and V). Layered materials are highly reactive with water, leading to the formation of Na_2CO_3 and NaOH on their surfaces, as well as the incorporation of water molecules or hydrogen ions at sodium ion sites. Fourier-transform infrared spectroscopy (FTIR) spectra of NFM, D-NFM, and D-NFM-W reveal that D-NFM-W, obtained after water separation, lacks characteristic peaks for hydrogen bonding, indicating that no water molecules are present between the transition metal layers (Fig. S3). The interlayer spacing of D-NFM-W is 0.53 nm, which is close to the interlayer distance observed when H^+ ions are intercalated. This suggests that after water separation, H^+ ions primarily occupy the sodium ion sites, providing charge compensation and maintaining the layered structure. This transformation likely results from intense reactions that dissolve surface transition metals, causing the rock-salt phase to disappear and the layered structure to collapse, forming a new spinel phase. The ICP results for the water solution after separation, presented in Table S3, reveal trace amounts of Ni, Fe, and Mn. This confirms that during the separation process, intense reactions caused the surface layers of the material particles to detach, leading to the disappearance of the rock-salt phase on the surface of the D-NFM-W material. This suggests that while the layered material maintains its primary structure after water exposure, there is still some structural degradation, particularly at the non-sodium transport interfaces.

Structural damage and replacement of Na with H inevitably affects the leaching performances of cathode materials. Initially, we try to remove all sodium from materials using water as the separating medium. If the sodium ions are entirely replaced by hydrogen, the remaining transition metal elements can dissolve without the need for precipitation separation, allowing the reaction solution to be used directly for material synthesis, thereby reducing energy and chemical consumption. Figure 3H and I show that water immersion effectively removes sodium ions from the material, with leaching efficiency increasing over time at 25 °C, approaching 79.6% after 24 h. Additionally, the leaching efficiency of sodium ions increases with temperature. At 60 °C, a 1-h immersion yields 78.4% efficiency. Prolonging the immersion time at 60 °C increases the leaching efficiency of sodium ions to about 80%. This means that the upper limit of sodium substitution of NFM material by hydrogen is about 80%.

The acid leaching is conducted on the cathode materials under the conditions of 5% H_2O_2 and 1 M H_2SO_4 solution, a solid-to-liquid ratio of 50 g l^{-1} , 60 °C, and 1 h. Figure 3J and K show the acid leaching results of materials with and without water treatment. For the D-NFM materials, water washing slightly reduced the sodium leaching efficiency to 89.3% due to the partial disruption of the layered structure. In contrast, for NFM materials, the acid leaching enhanced the sodium leaching efficiency, reaching up to 98.4%. Figure 3K reveals that water-separated materials exhibit decreased solubility in acid. The leaching rate of D-NFM materials reached 57.4%, while that of D-NFM-W drastically decreased to only 15.3% at 80 °C. This decrease may be attributed to hydrogen occupying the sodium ion sites after water leaching, resulting in a more stable material structure. Therefore, the water separation method modifies the material structure to some extent, promoting the reduction of transition metals and thereby inhibiting acid solubility. This limitation of acidic dissolution is disadvantageous for hydrometallurgical recovery, indicating a need for exploring more suitable leaching methods.

NFM regeneration

We regenerate the failed NFM by sodium supplementation and thermal treatment [35]. This approach replenishes the missing sodium ions and repairs the damaged structure. The recycled NFM materials soak in water for 1 h to better remove the surface CEI. After this, approximately 70% of sodium ions are extracted from the NFM. Therefore, we choose to add sodium sources (Na_2CO_3) in molar ratios of 65%, 70%, and 75%, followed by sintering at different temperatures for 10 h.

The XRD patterns for materials regenerated at different temperatures and with varying Na_2CO_3 contents at 900 °C are shown in Figs. S4 and S5. These patterns indicate that under all regeneration conditions, D-NFM-W is changed from the P3 phase to the O3 phase. This suggests that high-temperature treatment allows sodium ions to reinsert into the material, and the presence of strong characteristic peaks such as (003) and (104) confirms that the layered structure is well-preserved after regeneration. SEM images of materials regenerated at 900 °C with different Na_2CO_3 contents, presented in Fig. S6, reveal that the morphology of secondary particles in S-65, S-70, and S-75 remains unchanged. However, the surface of S-75 shows numerous additional particles, likely due to excess sodium carbonate residue, which is a key factor contributing to the decreased electrochemical performance of S-75.

To demonstrate the restored electrochemical performance of the cathode material after regeneration, half-cell tests are conducted within a voltage range of 1.5 to 4 V. The cycling performance of materials regenerated at different sintering temperatures is shown in Fig. 4A. It is observed that as the sintering temperature increases, the discharge capacity of the repaired materials improves. For the material regenerated at 900 °C, the discharge capacity at 1 C reaches 89.7 mAh g⁻¹. This improvement is attributed to the high temperature facilitating the insertion of sodium ions and providing more energy for the transition from P3 to O3. Subsequently, we investigated the effect of varying amounts of sodium carbonate added at 900 °C on the regenerated materials' performance, with the electrochemical performance detailed in Fig. 4B to F. The first cycle charge–discharge curves are shown in Fig. 4B. At a current density of 0.1 C, the NFM with 70% sodium replenishment (S-70%) exhibits the highest initial discharge capacity of 102.4 mAh g⁻¹, significantly higher than that of S-75% and S-65%. Additionally, S-70% shows an initial charge capacity of 109.4 mAh g⁻¹ with a coulombic efficiency of 93.6%.

The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) curves of the regenerated materials are shown in Fig. 4C and D. From the CV curves, both S-70% and S-75% exhibit 1 oxidation peak and 2 reduction peaks, similar to those of commercial NFM (C-NFM). The single oxidation peak corresponds to the transition from O3 to P3 phase, while the 2 reduction peaks correspond to the transitions from P3 to O'3 and O'3 to O3 phases [36]. Of note, the oxidation peak potential of the regenerated materials is higher than that of C-NFM. This increase is attributed to the incomplete incorporation of sodium ions from Na₂CO₃ into the layered structure, leading to a deficiency of sodium ions in the material and a subsequent rise in charging potential. Additionally, residual Na₂CO₃ on the surface influences

the interfacial charge transfer reactions, increasing the polarization potential. The S-70% exhibits low charge transfer resistance (R_{ct}), indicating that adding 70% sodium results in a uniform O3 phase without leaving residual Na₂CO₃ on the material surface (Fig. 4C), which can hinder sodium ion transport. This uniform phase contributes to its excellent electrochemical performance.

Long-cycle performance at 1 C is presented in Fig. 4E. The S-70% shows a discharge capacity of 89.5 mAh g⁻¹, which is lower than the 101.7 mAh g⁻¹ of C-NFM. However, after 100 cycles, S-70% maintained a discharge capacity of 81.6 mAh g⁻¹ with a capacity retention rate of 91.2%, whereas C-NFM's capacity dropped to 73.5 mAh g⁻¹, with a retention rate of 72.3%. Additionally, during the initial cycles, both S-70% and C-NFM exhibit nearly 100% coulombic efficiency, indicating fewer side reactions during the redox process. The rate performance, shown in Fig. 4F, reveals that S-70% significantly outperforms S-65% and S-75%. Specifically, S-70% achieves a specific capacity of 106.2, 97.1, 89.7, and 77.5 mAh g⁻¹ at 0.1, 0.5, 1, and 2 C, respectively. Furthermore, after cycling at different rates, the specific capacity of S-70% can recover to 105.4 mAh g⁻¹, close to its initial value, demonstrating its good cycle stability.

Environmental and economic analysis

Based on the aforementioned SIB recycling process and results, we calculate the consumption, environmental impact, and economic benefits from the battery disassembly, cathode separation, NFM leaching, and NFM regeneration. These results are compared with those of LIB recycling. Figure 5A and Fig. S8 illustrate the differences in the disassembly and recycling processes for SIBs and LIBs. The main differences lie in the separation of the cathode and the dissolution and purification of the separated materials. The processing of other materials is almost identical between the two.

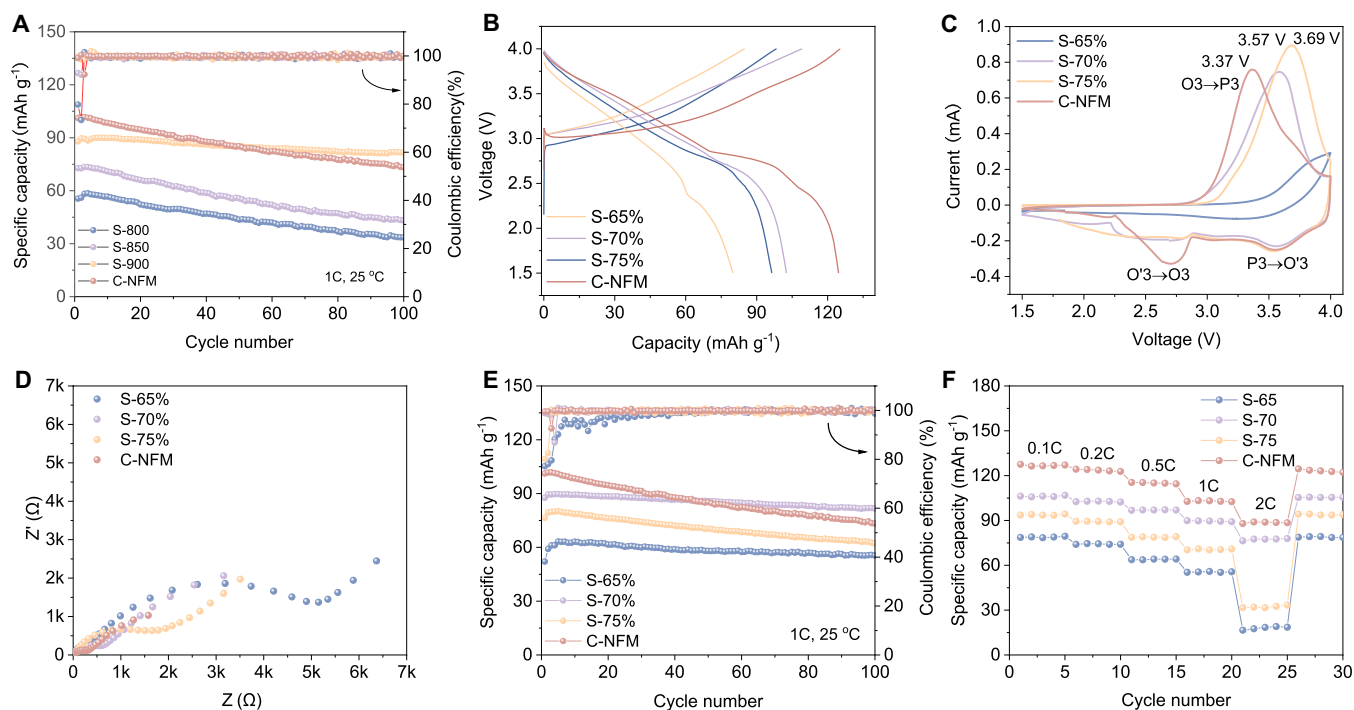


Fig. 4. (A) Cycling performances of regenerated NFM at different temperatures. (B) Voltage–capacity curves of regenerated NFM. (C) Cyclic voltammetry curves of regenerated NFM. (D) Impedance curves of regenerated NFM (the corresponding equivalent circuit diagram is shown in Fig. S7). (E) Cycling performances of regenerated NFM with different Na₂CO₃ contents. (F) Rate performance of regenerated NFM with different Na₂CO₃ contents.

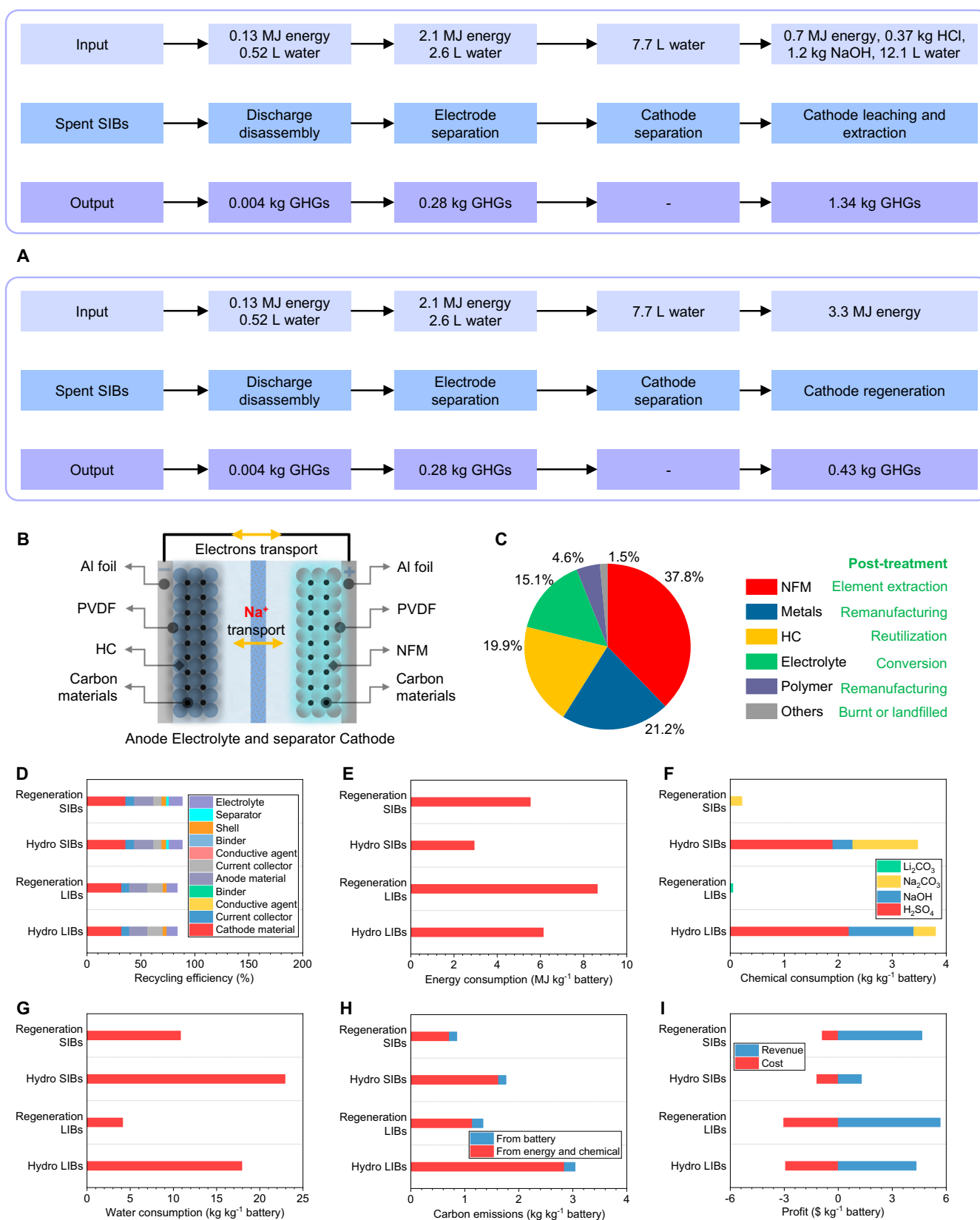


Fig. 5. (A) Process diagram of SIBs recycling. (B) Schematic diagram of SIBs. (C) Proportion of different materials in SIBs. (D) Recycling efficiency of LIB and SIB materials. (E) Energy consumption of LIB and SIB recycling. (F) Chemical consumption of LIB and SIB recycling. (G) Water consumption of LIB and SIB recycling. (H) Gas emissions of LIB and SIB recycling. (I) Profit of LIB and SIB recycling.

For ease of calculation and comparison, we select similar material systems and use realistic material ratios for LIBs and SIBs (Fig. 5B and C). Both are based on 1 kg of battery weight. The energy and chemical consumption, as well as the recovery efficiency for each recycling process, are based on previous publications [17,37]. The recycling rates for LIB anode and cathode materials and current collectors are calculated using an ideal recovery efficiency of 90%, while the separator and shell are considered at 100%, and the electrolyte at 80%. For SIBs, the recycling efficiencies are the same as those for LIBs, except for the cathode material and current collector, where our experimental recovery efficiency is about 95%. Based on the material ratios and recovery efficiencies for LIBs and SIBs, their total recycling efficiencies can reach up to 86.85% and 88.23%, respectively, approaching the ideal recovery values for these batteries (Fig. 5D and Table S4).

For the element extraction, the main energy consumption in the recycling process is from the thermal treatment of battery materials. For traditional LIB cathode separation, the electrode needs to be processed at 500 to 600 °C to burn off PVDF and SEI (solid electrolyte interphase) materials, making subsequent material separation and treatment much easier. In contrast, SIB recycling requires similar treatment only for the anode. Accounting for the mass ratio of materials treated thermally, the total energy consumption for LIB and SIB recycling, including other processes, is 6.13 and 2.93 MJ, respectively (Fig. 5E). Chemical reagents are another crucial aspect of the recycling process. For separated LIB cathode materials, inorganic acids are typically used for dissolution, followed by the use of extractants to remove impurities, separate transition metals, and precipitate lithium. This process consumes about 0.81 kg of HCl, 1.2 kg of NaOH, and 0.4 kg of Na_2CO_3 without considering the loss of theoretically reusable extractant and other materials (Fig. 5F). We assume that the extraction of transition metal elements from SIB cathodes requires the use of chemicals similar to those used for LIB cathodes, leading to the consumption of 0.37 kg of HCl and 1.2 kg of NaOH. Additionally, SIB recycling requires 2 l more water compared to LIB recycling due to more intensive water use during cathode separation (Fig. 5G). Ideally, the 7.7 l of water used in SIB cathode separation can be reused because the aqueous solution mainly contains NaOH. Therefore, the overall water consumption in SIB recycling can be reduced. When energy consumption and chemical usage are converted into carbon emissions, SIB recycling generates approximately 1.76 kg of CO_2 (Fig. 5H). This is significantly lower than the 2.95 kg of CO_2 produced by LIB recycling, primarily due to the higher chemical consumption in the LIB process.

Based on the investment in the battery recycling line, material consumption, and the value of recovered materials, we calculate the cost and revenue [17,38]. The equipment investment for recycling SIBs and LIBs is the same, while it is different in the battery fee and the cost of chemicals. Spent LIBs need to be purchased for approximately \$1.50 due to their high content of valuable metals. In contrast, SIBs contain fewer valuable metals, making them less attractive to recycling plants. In some cases, treatment of spent SIBs might even require a fee for consumers or battery manufacturers. The total cost used in the recycling process is \$3.10 for LIBs and \$1.33 for SIBs (Fig. 5I). The value of recovered materials is calculated based on projected market prices. In particular, we value recovered lithium at $\$75 \text{ kg}^{-1}$ and recovered carbon materials at $\$1 \text{ kg}^{-1}$. The total value of recovered materials is \$1.29 for SIBs and \$4.33 for LIBs.

Subtracting the costs from the revenue, the profit is \$0.10 for SIBs and \$1.40 for LIBs, demonstrating that element extraction from SIBs is not cost-effective.

We calculated the consumption and profit of the cathode material regeneration. The difference between material and element extraction for SIBs lies only in the final material treatment. During the regeneration process, the material requires only a thermal treatment at 900 °C with a 70% molar ratio of Na_2CO_3 , eliminating the need for material dissolution and extraction. This significantly reduces material consumption and adds only 3.3 MJ of energy to the process. Consequently, the energy consumption, chemical consumption, water consumption, and CO_2 emissions for cathode material regeneration are 5.73 MJ, 1.61 kg of Na_2CO_3 , 10.82 l, and 0.85 kg of CO_2 , respectively, making it highly competitive compared to element extraction. Due to the higher value of the regenerated material, the revenue is as high as \$4.64 with a cost of \$0.89, resulting in a profit of \$3.76, which is even higher than the \$2.64 profit from LIB recycling. This is mainly due to the absence of a purchase price for spent SIBs and the relatively lower process consumption.

Conclusion

This work is the first investigation of spent SIB. It is discovered that water can effectively separate the cathode material from the current collector. This separation method is simple and efficient and produces minimal pollution, offering a potential route for the pretreatment of SIBs. Contact with water further collapses the cathode material structure, with intense sodium ion extraction reactions causing numerous cracks. Meanwhile, the interface forms a complex layer of 5- to 10-nm rock-salt and spinel phases. Following water separation, the H/Na exchange inhibits the material's reactivity, leading to reduced efficiency in transition metal dissolution. This presents significant challenges for the hydrometallurgical recovery of water-separated materials. However, the bulk material after water separation contains minimal impurities and the layer structure remains, facilitating material regeneration. Owing to the significantly lower cost of SIB recycling and the material price of SIBs being almost similar to that of LIBs, the profitability of SIB recycling is even higher than that of LIB recycling.

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Competing interests: The authors declare that they have no competing interests.

Data Availability

All data are available from the corresponding authors upon reasonable request.

Supplementary Materials

Figs. S1 to S8
Tables S1 to S4

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