Green Recovery of Cathode Active Materials from Li-ion Battery Electrode Scraps using Propylene Carbonate: A Novel Approach for Direct Recycling

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Abstract

Retrieving cathode active materials from Li-ion battery electrode scraps is a crucial step in direct recycling; however, it presents challenges due to the strong bonds between the active material, carbon black, and binder. In this work, we propose the use of propylene carbonate (PC) as a green solvent for a solvent-based liberation/separation process. Compared to other green solvents, PC offers the advantage of efficiently liberating active materials from electrode scraps at a relatively low temperature and within a short time. The reclaimed cathode obtained through the PC-based process retains its morphological, structural, and electrochemical characteristics, demonstrating the suitability of the developed process for direct recycling. Additionally, the process provides an intriguing benefit by enhancing the charge transfer resistance of the reclaimed active material. The use of PC in the solvent liberation/separation process offers a viable approach to mitigate impurity-related challenges commonly encountered in solvent-based processes. By leveraging the plasticizer effect of PC, the residual PVDF species on the active material are transformed into species that facilitate Li-ion conduction. This transformation leads to an improvement in the overall electrochemical performance of the recovered cathode material.

Keywords: Propylene Carbonate, Separation, Delamination, Direct Recycling, Electrode Scrap, Binder Dissolution, Plasticizer, End-Of-Life Batteries.

Introduction

Due to the significant growth of the electric vehicle (EV) market, there is a need for efficient management of end-of-life (EOL) battery cells and electrode scraps through green and profitable recycling or appropriate disposal processes.[1-4] This is crucial as the production of a huge number of Li-ion batteries (LIBs) is expected to meet the demands of the EV industry, while also addressing environmental concerns and supply chain issues. Consequently, the development of cost-effective recycling processes for EOL batteries and electrodes is essential to establish a circular battery economy, thereby enhancing the sustainability of EV batteries.[3, 4]

Among the various components of spent LIBs, the cathode material holds the highest value as it determines the battery's price, weight, and energy density.[5] Current recycling methods, including pyrometallurgical, hydrometallurgical, and direct recycling techniques, have primarily focused on the recycling or reuse of cathode materials.[6-11] Direct recycling, in particular, is widely favored in academic and industry due to its accessibility and significant economic benefits.[1, 3, 12, 13] This process aims to restore the functionality of the spent cathode material by reintroducing lithium into its crystal structure without breaking down the original structure. A crucial step in direct recycling is the liberation/separation process, which involves recovering valuable cathode active materials while effectively treating the binder, polyvinylidene fluoride (PVDF), present in spent electrodes. Given the environmental concerns associated with halogen-containing electronic waste, appropriate removal of fluorine-bearing PVDF from spent LIBs is imperative.[14]

The cathode active material is strongly bonded to each other and the aluminum (Al) foil via the PVDF binder. The strong bonds between the cathode active material, the PVDF binder, and the Al foil pose a challenge in their effective separation while preserving their functional structures. However, this issue can be overcome by employing a solvent-based method that enables the recovery of cathode active materials without compromising their morphological and chemical characteristics.[15-19] Dissolving and deactivating the PVDF binder in solvents is not a straightforward process due to the excellent chemical resistance and high-temperature stability of PVDF.[14, 20] Therefore, the selection of an appropriate solvent is critical to ensure the extraction of pure cathode materials without introducing any impurities, while also optimizing the process in terms of time and temperature.[17]

Dipolar aprotic organic solvents, such as N-methyl pyrrolidone (NMP) and N, N-dimethylformamide (DMF), are commonly used in solvent-based separation methods to dissolve the PDVF binder and recover cathode materials.[21-23] NMP effectively disrupts the strong interchain bonds in the PVDF crystal structure and weakens the polymer's attachment to the Al foil without causing any molecular or microstructure changes.[23] However, it is important to note that NMP and DMF are classified as restricted organic substances under the Registration, Evaluation, and Authorization of Chemicals (REACH) due to their adverse effects on human health and the environment.[24, 25] Therefore, their large-scale usage should be minimized.[24, 25]

Recently, alternative solvents that are safer and more environment-friendly have been proposed for sustainable cathode delamination. These include ethylene glycol (EG), triethyl phosphate (TEP), and cyrene.[15-18] While EG can achieve complete cathode delamination at high temperatures, it may make the separation of PVDF from the cathode active material challenging.[17] On the other hand, cyrene, although effective, is relatively expensive compared to other solvents (**Table 1**), which reduces its cost-effectiveness for cathode separation. TEP, despite having flash and boiling points similar to EG, may not be a sustainable option for cathode recycling over time due to its extensive use in various industrial sectors, contributing to the depletion of phosphorus from the earth's crust. [26]

Table 1. Physical properties and hazard statements for different solvents used in the literature.[25] The hazard statement associated with the solvents were derived from their respective Material Safety Data Sheets (MSDSs).

Solvents	FP (°C)	BP (°C)	Hazard Statements		S/H/E scores	Price
NMP	91	202	⚠ ◆	**H315, H319, H335, H360D**	🟩 1 🟥 9 🟥 7	Moderate
DMF	58	153	⚠ ◆	**H226, H312+H332, H319, H360D**	🟩 3 🟥 9 🟨 5	Moderate
EG	116	198	⚠ ◆	**H302, H373**	🟩 1 🟩 2 🟨 5	Good
TEP*	115	216	⚠	**H302, H319**	N/A	Good
Cyrene*	61	203	⚠	**H319**	🟩 1 🟩 2 🟥 7	Expensive
PC*	132	242	⚠	**H315, H319, H335**	🟩 1 🟩 2 🟥 7	Good

* Green solvents, FP=Flash point, BP=Boiling point, S/H/E=Safety/Health/Environment

In this study, we propose the utilization of propylene carbonate (PC) as a safer and more sustainable alternative to toxic solvents like NMP and DMF for the recovery of cathode active materials from EOL electrodes and electrode scraps. PC is a polar, aprotic solvent with low toxicity and possesses a higher boiling point and lower vapor pressure compared to other green solvents (**Table 1**).[27] These physical properties of PC are advantageous in reducing the risk of adverse health effects, minimizing solvent loss or emission, and enhancing safe handling and operation for battery recycling applications. Moreover, PC is biodegradable and economically viable, making it suitable for large-scale applications. Its use in the Li-ion battery recycling process has the potential to reduce pollution and minimize the environmental footprint associated with solvent use.[27, 28] PC is a CO_2-based "carbon-sequestering" solvent that can be degraded by certain microorganisms.[28] Recycling PC after its use in the battery recycling process is feasible, as it can degrade and return to the natural carbon cycle more rapidly compared to non-biodegradable solvents.

Although the solubility parameters of PC, such as the Hansen and Hildebrand parameters, suggest relatively lower solubility of PVDF compared to other solvents used in previous studies (**Table S1**), our experimental results indicate that PC demonstrates a high capacity for PVDF dissolution at specific temperatures. It should be noted that the Hansen and Hildebrand parameters offer limited accuracy (60–67%) in predicting polymer solubility.[29] Polymer solubility in solvents is a complex process influenced by various factors, including chemical, morphological, thermodynamic, and kinetic considerations, which are interconnected.[29]

In this study, we developed a PC-based liberation/separation process that operates at a comparatively lower temperature than other solvent-based methods. The effectiveness of our developed process was assessed by conducting cathode delamination tests with different electrode types and comparing the results with those obtained using other green solvents. We also discussed the potential mechanisms underlying the dissolution and deactivation mechanisms of PVDF in PC. The recovered cathode active material demonstrated preserved functional characteristics, retaining its original morphology, chemical structure, and electrochemical reactivity. Consequently, the recovered material exhibited comparable reversible capacity and electrochemical performance to that of the original cathode material. To the best of our knowledge, this is the first report on the application of PC in the cathode liberation/separation process. Our findings suggest that PC can not only serve as an electrolyte for LIBs but also be employed as a sustainable solvent for direct LIB recycling.

Experimental

Materials. In this study, a new $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) industrial-grade electrode (MTI Corp.) was mainly used. The areal loading of the NMC532 cathode was approximately 11.4 mg/cm^2, comprising 94.2% of the active material. To systematically evaluate the efficiency of the PC-based liberation/separation process, a spent cathode electrode (NMC532/$LiMn_2O_4$) obtained from a battery cell with 80% state of health (SOH) was utilized, along with a laboratory-made NMC532 electrode. The lab-made electrode consisted of NMC532 (MTI Corp.), carbon additives (C65 and KS6L, Imerys), and PVDF binder (W#7200, Kureha) in a weight ratio of approximately 94.3:3. PC (> 99.7 %, Sigma Aldrich), triethyl phosphate (> 98 %, Alfa Aesar), ethylene glycol (99.5 %, Acros Organics), and n-methyl-2-pyrrolidine (anhydrous, > 99 %, Sigma-Aldrich) were used without any treatment.

PC-based liberation/separation process. The developed PC-based liberation/separation process is illustrated in the schematic flowchart shown in **Figure 1a**. First, an industrial-grade NMC 532 electrode sheet was manually cut into several pieces (2.54 × 2.54 cm). These pieces were then immersed into 200 mL of PC solvent at a temperature of 80 °C and stirred for 5 minutes. Subsequently, the electrode-solution mixture was subjected to sonication for 1 minute, resulting in the liberation of the majority of the active material and carbon additive from the Al foil (**Fig. 1b**). Following liberation, the black-colored solution was subjected to centrifugation and washed three times to remove the carbon additive and PVDF binder. During the centrifugation process, the density differences between carbon black and NMC were utilized for their separation. The centrifugation caused the denser material, NMC, to sediment and form a compact pellet or layer at the bottom of the container or on the wall. Simultaneously, the less dense material, carbon black, remained suspended in the solution. The centrifugation process was repeated until the black-color solution turned transparent. Finally, the recovered powder was filtered and vacuum-dried overnight at 100 °C.

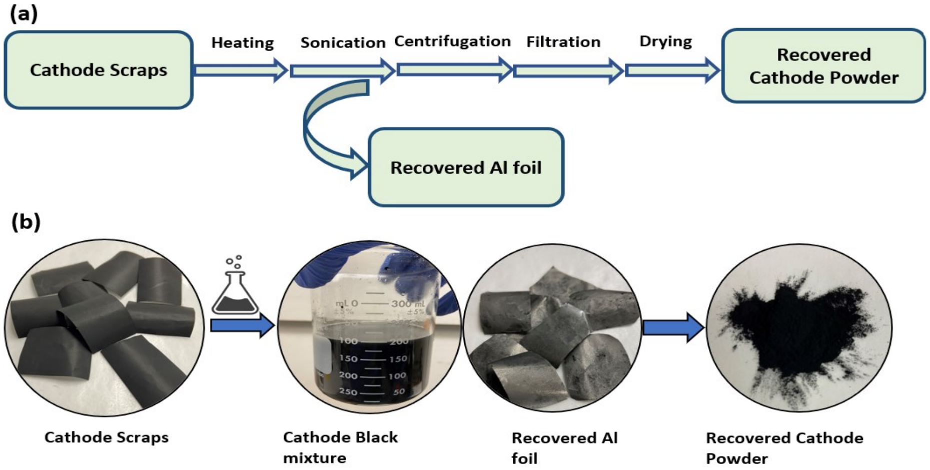


Fig. 1. (a) Schematic flowchart of the PC-based liberation/separation process and (b) photos showing cathode scraps, black mass in PC, recovered Al foil, and recovered NMC532 powder.

Materials characterization. The reclaimed NMC532 powder and Al foils were subjected to various characterization techniques to analyze their surface morphology, phase, crystallinity, and composition. Scanning electron microscopy (SEM, JEOL 7800f, Tokyo, Japan) equipped with energy-dispersive X-ray spectroscopy (EDX) was used to examine the surface morphology and composition. X-ray diffraction (XRD, Bruker D8 Discover, USA) was employed to determine the phase and crystallinity. XRD measurements were conducted over a 2θ angle range of 10°–70° at a scanning rate of 0.85°/min. Thermogravimetric analysis (TGA, TA instruments SDT-Q600, New Castle, DE, USA) was carried out to investigate the composition and thermal stability of the samples. TGA measurements were performed at a ramping rate of 5 °C/min in an argon flow (50 mL/min) over a temperature range of 25–800 °C. The characteristics of the recovered NMC532 samples were compared with those of the fresh NMC532 electrode and powder.

Cell fabrication and electrochemical measurements. The recovered NMC532 powder (94.2 wt.%) obtained from the industrial-grade electrode was mixed with carbon additives (2.9 wt.%, KS6L, and C65) and PVDF binder (2.9 wt.%, Kureha 7200) to form a slurry. The resulting slurry was then coated onto Al foil using a doctor blade. The coated electrode was subsequently vacuum-dried overnight at 120 °C. To achieve the thickness of the industrial-grade NMC electrode, the dried electrode was calendared. The areal loading of the fabricated electrode was approximately 12.0 mg/cm^2, which closely matched the target loading of 11.4 mg/cm^2. For electrochemical tests, coin cells were assembled in a half-cell configuration (recovered NMC532 electrode vs. Li counter/reference electrode) in an Ar-filled glove box. The electrolyte used was a 1.2 M solution of $LiPF_6$ in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with a volume ratio of 1:1 (Sigma Aldrich). The cells were rested for 12 h and then subjected to 5 charge/discharge cycles at a C/10 rate using a constant current/voltage (CC-CV) charge and a constant current (CC) discharge protocol, followed by 100 cycles at a C/3 rate using a CC charge and discharge protocol. The cells were cycled within a potential range of 3.0-4.2V (Li/Li^+). Electrochemical impedance spectroscopy (EIS) tests were conducted after 5 and 105 cycles in the fully discharged state (i.e., 3.0 V vs. Li/Li^+) by applying a 5 mV amplitude perturbation over a frequency range of 500 kHz to 0.1 Hz.

Results and Discussion

PC-based liberation/separation process. PC is considered a latent solvent for PVDF polymer, meaning it is unable to dissolve PVDF at room temperature due to the entanglement of the polymer chains and the weak interaction between PVDF and PC.[30] However, when the temperature is increased, the PVDF polymer chains start to swell, allowing PC to diffuse rapidly into the PVDF crystalline structure, leading to PVDF dissolution.[31] Previous studies have shown that direct cathode liberation/separation using green solvents typically requires high temperatures (≥ 100 °C) to induce the swelling of the PVDF polymer chains through fast solvent diffusion.[15-19] However, the use of high temperatures for direct cathode recovery comes with increased energy consumption, which raises concerns regarding safety and processing costs. Therefore, it is desirable to develop a solvent-based liberation/separation process that enables PVDF dissolution at lower temperatures (< 100 °C) using a green solvent.

In this study, the PC-based liberation/separation process was demonstrated to be effective at a relatively low temperature of 80 °C (**Fig. 2a**). At this temperature, PC facilitated the swelling of PVDF chains, enabling efficient delamination of the cathode coating from the Al foil. It is important to note that a short sonication process was necessary to completely break down the weakened bond between the cathode coating and the Al foil. Interestingly, increasing the sonication time did not significantly enhance the delamination efficiency. For instance, when the liberation was performed at a lower temperature of 60 °C, complete cathode delamination was not achieved, resulting in a lower liberation efficiency of ~ 26%, after 1 hour of stirring and 6 minutes of sonication. This suggests that the efficiency of the PC-based process is dependent on the stirring temperature and duration, and sufficient heat is required to activate the interaction between PVDF and PC. Based on our test results, the optimal processing temperature for the PC-based liberation/separation process was determined to be 80 °C.

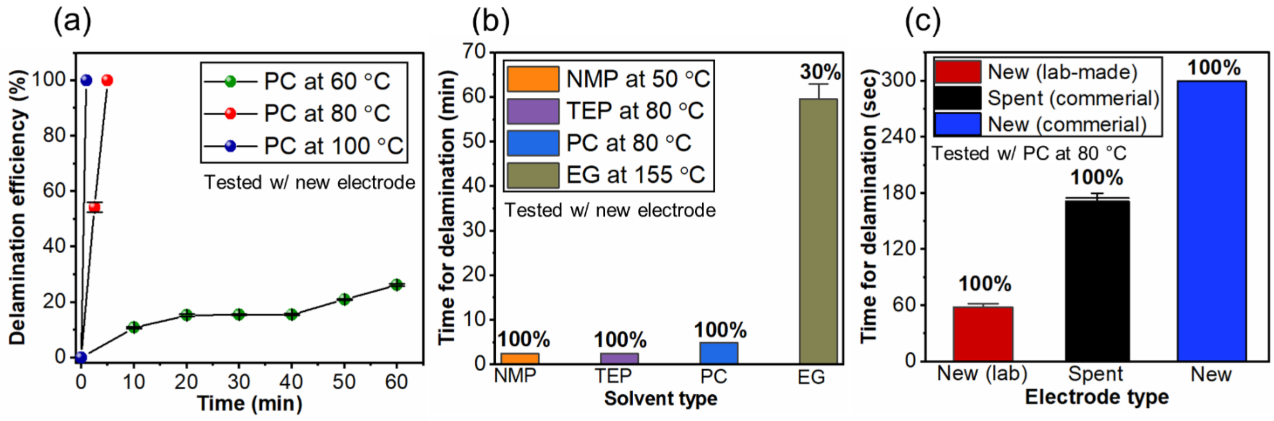


Fig. 2. Comparison of cathode delamination efficiency: (a) with PC at different temperatures; (b) with different solvents; (c) with different types of electrodes using PC. Unless noted otherwise, all experiments were performed with the new industrial-grade NMC electrode. The efficiency of cathode delamination was estimated by measuring the weight of the Al current collector after the liberation process. The mass of cathode coating (active material, binder, and carbon black) liberated from the Al current collector was compared before/after the process. The recovery of the active material from the delaminated cathode coating was approximately 70% for the PC-based process.

To compare the effectiveness of the PC-based process, we also applied similar processes using NMP and other green solvents, such as TEP and EG,[16, 17] to delaminate the same industrial-grade NMC electrode (**Fig. 2b**). NMP, known for its ability to dissolve PVDF at room temperature, successfully delaminated the cathode coating completely from the Al foil within a short time (~3 min stirring at 50 °C followed by 1 min sonication). Similarly, TEP was highly effective in delaminating the cathode coating, achieving complete delamination with approximately 3 min of stirring at 80 °C followed by 1 min of sonication. However, EG did not achieve complete cathode delamination, even at a high temperature (155 °C). It only showed a delamination efficiency of about 30% after processing for 1 hour. This result was inconsistent with a previous report where EG was reported to liberate the cathode coating within a few minutes.[17] This discrepancy could be due to the strong PVDF-Al foil bond in the new electrode used in this study or the differences in the liberation procedure compared to the previous study.

Furthermore, we evaluated the PC-based process using different grades of electrodes. As shown in **Fig. 2c**, the time required for complete delamination varied significantly depending on the electrode grade. The new industrial-grade NMC electrode, which was mainly used in this study, took a longer time (298 sec) for complete delamination compared to other types of electrodes. For instance, the lab-made electrode required only 60 sec for complete delamination. This indicates that the electrode manufacturing process significantly affects the bond between the cathode coating and the Al foil through the PVDF binder, resulting in different delamination times. Additionally, the spent NMC electrode (industrial-grade), which had undergone repeated cycling, was completely delaminated in approximately 178 sec, demonstrating a higher liberation efficiency compared to the new industrial-grade NMC electrode. This can be attributed to the weaker adhesion strength between the cathode coating and Al foil in the spent electrode due to the electrode stress caused by the expansion and shrinkage of the cathode active material during cycling.[32-34]

Overall, the PC-based liberation process showed effective delamination of different types of electrodes within a short period of time. The liberation efficiency was comparable with TEP- or NMP-based processes but significantly higher than the EG-based process. More importantly, the PC-based process required a relatively lower temperature to reclaim the cathode material compared to other green solvents that were previously studied.[15, 17, 19]

PVDF dissolution and cathode delamination mechanisms. Dipolar aprotic solvents, including NMP, DMF, TEP, dimethylsulfoxide (DMSO), trimethyl phosphate (TMP), and dimethylacetamide (DMAc), have been identified to dissolve PVDF polymer at 60 °C.[31, 35] PC is also considered a dipolar, aprotic solvent that could dissolve PVDF at a certain temperature. Nevertheless, the solubility of PVDF in PC has not been extensively studied, possibly due to the lower solubility power of PC compared to other solvents based on the Hansen solubility parameters (**Table S1**). PVDF dissolution in solvents is a complex process influenced by thermodynamic factors (such as enthalpy and entropy of mixing) and kinetic effects.[31] Although the Hansen parameters can help in selecting suitable solvents for PVDF dissolution, they may not accurately predict the solubility degree of PVDF in solvents, particularly at elevated temperatures.[29]

To gain insights into the mechanism of PC-based liberation, PVDF solubility tests were conducted using PC at different temperatures (**Fig. S1**). Even after 6 h of continuous stirring at 60 °C, the PVDF (10 wt%)-PC mixture solution remained clear, with some white-colored PVDF sediment at the bottom. This indicates that PVDF was not completely dissolved but instead precipitated as a crystalline substance upon cooling. It suggests inadequate breakdown of PVDF polymer interchains and limited PVDF-PC interaction at 60 °C. In contrast, when the mixture solution was stirred at 80 °C for 6 h, a shallow yellow color was observed without any PVDF sediment. This indicates that PVDF decomposition and dissolution occurred at 80 °C by reducing the interchain interaction of the polymer through PC penetration into the PVDF crystalline structure.[15]

The mechanism of PVDF dissolution at elevated temperatures can be explained by two main phenomena: (1) PVDF polymer chain disentanglement (**Fig. 3a**) and (2) disruption of PVDF polymer interchain links due to cross-linking of hydrogen bonds (**Fig. 3b**).[15, 19, 31, 36] As illustrated by the schematic of **Fig. 3a**, at room temperature, the entanglement of PVDF polymer chains hinders the diffusion of PC into the crystalline polymer structure.[31, 35] However, at 60 °C, enhanced PC diffusion leads to the swelling of the PVDF polymer structure without noticeable dissolution. When the temperature reaches a sufficient temperature of 80 °C, PC penetration into the PVDF polymer chains is facilitated, resulting in a considerable acceleration of polymer structure swelling. Eventually, the PVDF polymer interchain interactions are deactivated and decomposed, causing a change in the color of the PVDF-PC solution (**Fig. S1b**).

Heating PVDF in PC not only disentangles the polymer chains but also enhances the PC-PVDF interaction. As PC solvent molecules diffuse and expand the PVDF polymer structure, more sites for solvent-polymer interaction are created. This increases the likelihood of establishing cross-linking hydrogen bonds between the H atoms in PVDF and the O atoms of the carbonyl groups in PC (**Fig. 3b**).[15] The carbonyl group (-C=O) in PC is regarded as an electron-withdrawing group due to the higher electronegativity of the oxygen atom compared to carbon. This electronegativity difference creates a partial negative charge on the carbonyl oxygen atom, enabling it to accept a proton (H^+) from a hydrogen bond donor and participate in hydrogen bonding. Consequently, the carbonyl group in PC can form hydrogen bonds with the hydrogen atoms in PVDF.

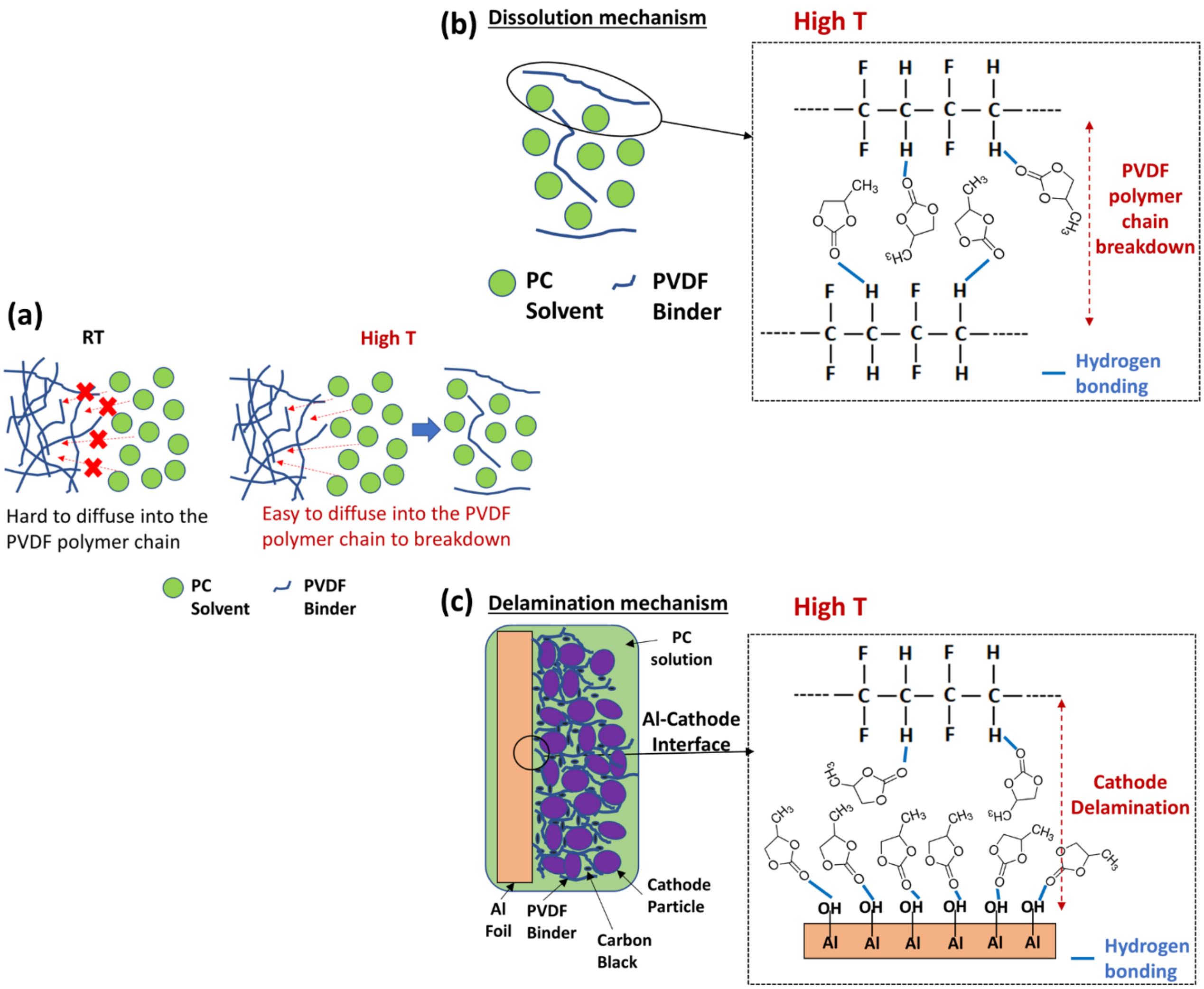
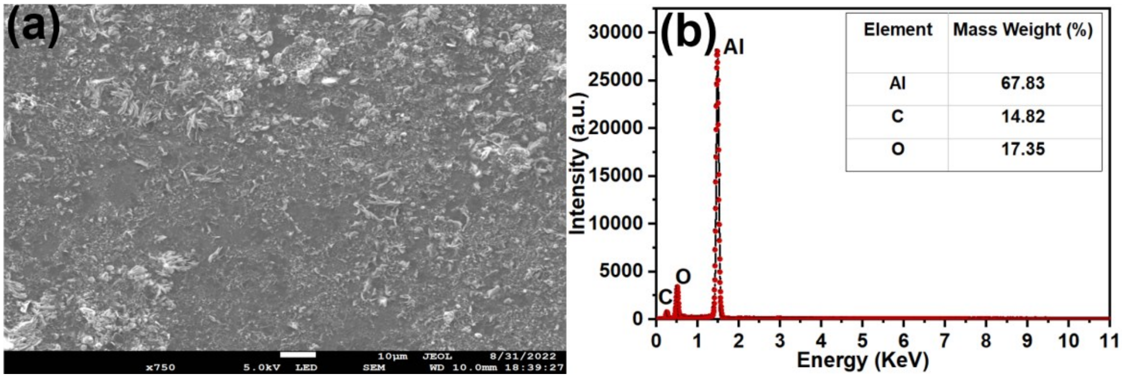


Fig. 3. A schematic of the mechanisms underlying the PC-based liberation/separation process: (a) PVDF dissolution via the polymer chain disentanglement at elevated temperature. (b) PVDF dissolution by enhancing the solvent-polymer interaction via cross-linking of hydrogen bonds. (c) Cathode coating delamination via cross-linking of hydrogen bonds between the O atoms in PC and the H atoms in the hydroxyl groups of the Al current collector.

The dissolution and decomposition of the PVDF binder weaken the adhesion strength between the cathode coating and the Al current collector. PVDF is eventually deactivated, leading to the liberation of the active material and carbon black from the electrode and the separation of active material particles from each other. Additionally, cathode delamination occurs through the cross-linking of hydrogen bonds between the O atoms in PC and the H atoms of the hydroxyl groups (-OH-) on the surface of the Al current collector (**Fig. 3c**). The Al current collector can possess hydroxyl groups on its surface when exposed to moisture and humid environments. A thin layer of adsorbed water molecules can form aluminum hydroxide ($Al(OH)_3$) on the surface. Alternatively, the hydroxyl group could form on the surface of Al when it is exposed to certain solvents at high temperatures.

The hydrogen bonding mechanism between the Al surface and PC was further supported by characterizing the Al foil after the PC-based liberation/separation process. The recovered Al foil did not show any active material particles on its surface, confirming successful cathode delamination from the Al foil (**Fig. 4**). Ni, Mn, and Co elements were not observed in the EDAX spectra. Furthermore, the absence of F element in the EDAX spectra suggested the absence of the original PVDF binder on the Al surface. Interestingly, a small amount of C and O elements was identified on the Al surface, which could originate from adsorbed PC molecules strongly adhered to the surface. Indeed, the recovered Al foil appeared a blackish or grayish color possibly due to oxidation upon its exposure to high temperature and/or possible reactions with PC molecules during the liberation/separation process. These observations align with the proposed mechanism of cathode delamination through the cross-linking of hydrogen bonds. This delamination mechanism is similar to the mechanism observed in EG-based delamination process.[17]



Element	Mass Weight (%)
Al	67.83
C	14.82
O	17.35

Fig. 4. (a) SEM and the corresponding (b) EDX spectra of the recovered Al foil after PC-based liberation/separation.

Characterization of the PC-recovered cathode material. As described above, the PC-based process successfully liberated the active material from the electrode. To separate the active material from the liberated solid mixture, the process involved a series of conventional steps:

centrifugation, filtration, and drying (**Fig. 1**). The collected active material was subjected to characterization to evaluate its morphology, chemical composition, phase, crystallinity, and purity.

The PC-based liberation/separation process was non-destructive and did not alter the morphology and chemical composition of the active material, making it suitable for direct cathode recycling (**Fig. 5**). SEM analysis of the recovered NMC particles showed that their morphology remained unchanged after the PC-based process. The EDAX spectra confirmed that there was no leaching of transition metals during the process. The recovered NMC532 material maintained the original ratio of Ni, Mn, and Co (5:3:2) after the process (**Table S2**). This indicates that the chemical composition of the active material was well-preserved, ensuring that the desired stoichiometry of the NMC532 material was maintained.

Although the PC-based process is non-destructive and maintains the integrity of the active material, complete removal of impurities and achieving a pure NMC active material was challenging, as observed in other solvent-based processes.[16-19, 23] Some residue, including carbon black, PVDF, and polymerized or adsorbed PC substances, remained adhered to the NMC particles (**Fig. 5e** and **Fig. S2**) after the process. While significant amounts of carbon black and PVDF were removed from the recovered NMC material, a small amount of residue still persisted (**Fig. 5f**). The presence of C and F elements in the recovered NMC indicated the presence of carbon black and PVDF residues. However, some residue could be associated with PC molecules adsorbed on or polymerized with the PVDF polymer chains. Since PC acts as not only a dissolving medium but also a plasticizer for polymers,[37-41] the gel-like substance residue adhered to NMC particles, which mainly consisted of C and O elements, could be formed due to the plasticizer effect of PC (**Fig. S2**). This was further supported by the increase in the amount of O in the recovered NMC material (**Fig. 5f**) and the presence of C and O on the Al current collector (**Fig. 4**).

It is worth noting that the residual substance, PC-associated compounds, had a positive influence on the electrochemical performance of the recovered cathode. The plasticizer effect of PC contributed to enhancing the electrochemical performance. The positive impact of the residual PC substance on the recovered cathode will be further elaborated in a separate section below.

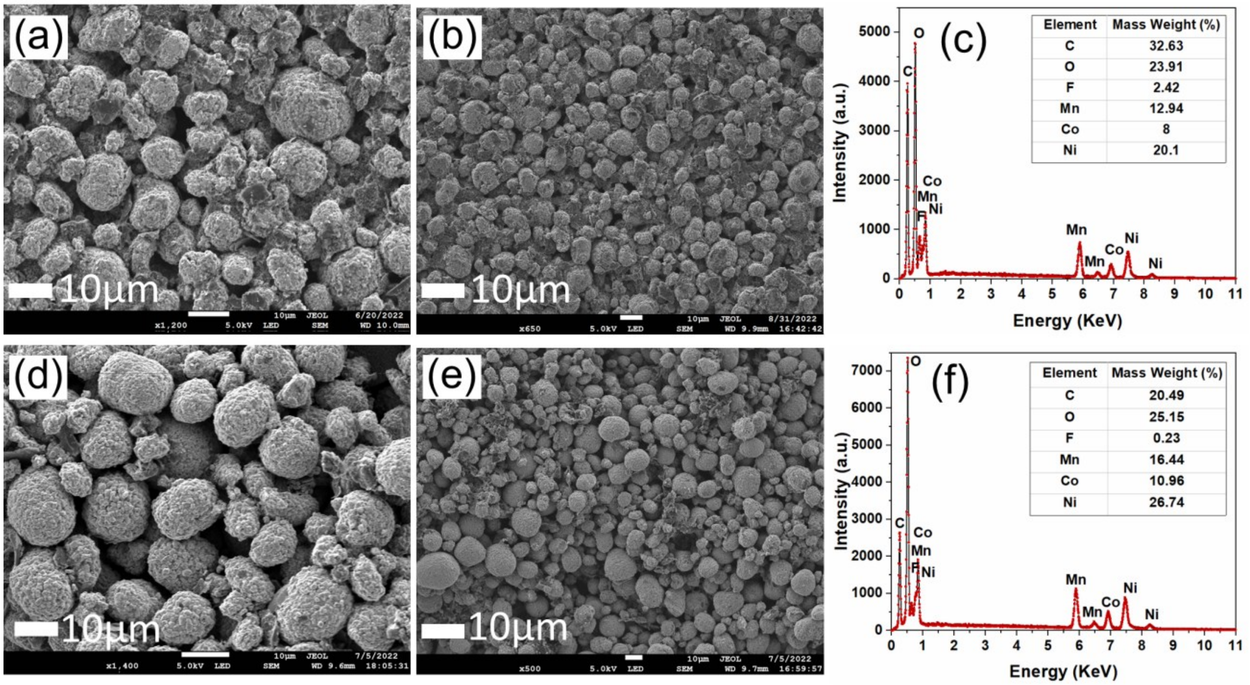


Fig. 5. SEM images showing the morphology of the NMC532 cathode (a), (b) before and (d), (e) after PC-based liberation/separation process; EDX spectra of the NMC532 cathode (c) before and (f) after PC-based liberation separation process.

The XRD patterns of the raw and recovered NMC powders were also compared to assess the crystal structure of the PC-recovered cathode material (**Fig. 6a)**. The diffraction peaks of both the raw and recovered powders were indexed to the R3m space group with the α-NaFeO$_2$ layered rhombohedral structure, indicating that the crystal structure of the reclaimed NMC powder was well preserved during the PC-based liberation/separation process. No significant peak shifting or broadening was observed in the XRD pattern of the recovered NMC, further confirming the preservation of the crystal structure. This suggests that the PC-based process did not introduce significant changes or defects in the crystal lattice of the recovered NMC powder.

Additionally, the intensity ratio of the (003)/(104) peaks (i.e., the I_{003}/I_{104}) did not decrease after the PC-based process (**Table S3**). The unchanged intensity ratio indicates that the PC-based process did not lead to a deterioration in the crystallinity of the recovered NMC material.[42] Moreover, the unchanged ratio also suggests that no cation mixing or lithium deficiency occurred in the reclaimed NMC material.[42]

However, it should be noted that a small XRD peak at approximately 26.6° was observed in the recovered NMC powder. This peak is attributed to the presence of carbon residues on the surface of the reclaimed NMC. While efforts were made to separate carbon black residue during the PC-based process, complete removal of all residual carbon proved challenging due to the presence of the gel-like substance associated with PC.

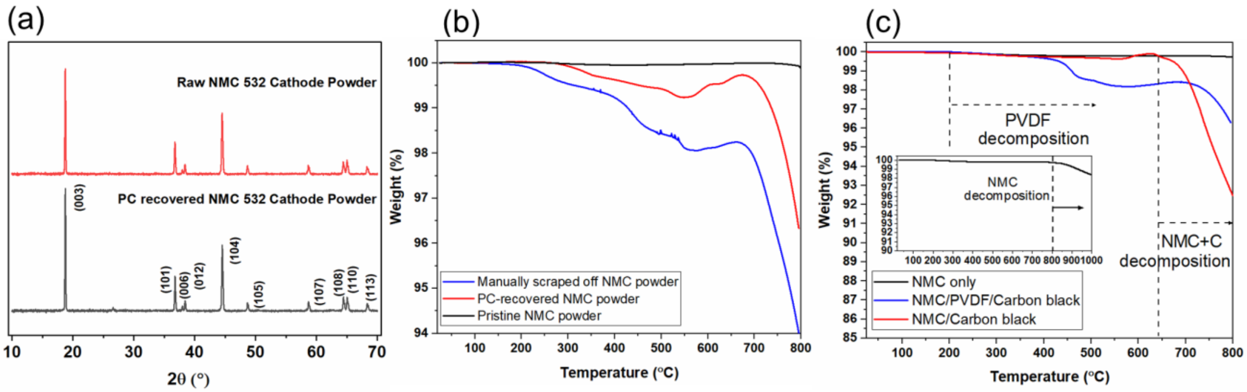


Fig. 6. (a) XRD patterns of pristine and recovered samples. (b) TGA comparison of pristine, PC-recovered, manually scraped-off samples. (c) TGA comparison of NMC powder, NMC/PVDF/carbon black mixture (94:3:3 wt.%) powders, and NMC/carbon black mixture powders (94:6 wt.%).

To further understand the residue substance on the surface of the reclaimed NMC, TGA was performed on pristine, manually scraped-off, and PC-recovered NMC powders (**Fig. 6b**). As expected, the pristine NMC powder, without any carbon black, showed no weight loss up to 800 °C. This means that the NMC material itself is stable and does not undergo significant decomposition in the absence of carbon black. In contrast, both the PC-recovered and manually scraped-off NMC powders displayed a significant weight loss starting at approximately 650 – 700°C. This weight loss is attributed to the decomposition reaction of NMC in the presence of carbon black, as described by **Eq. (1)**.[43]

$$4\ LiMeO_2 + 3\ C \rightarrow 2\ Li_2CO_3 + 4\ MeO + CO_2 \tag{1}$$

where Me represents transition metals including Ni, Mn, and Co. The decomposition reaction leads to the formation of Li_2CO_3 and MeO and the release of CO_2. Upon the reaction of NMC with carbon at elevated temperatures, the following reactions can take place subsequently:[43, 44]

$$Li_2CO_3 \rightarrow Li_2O + CO_2 \tag{2}$$

$$4\ MeO + 2\ C \rightarrow 4\ Me + 2\ CO \tag{3}$$

$$4\ MeO + 2\ CO \rightarrow 4\ Me + 2\ CO_2 \tag{4}$$

The decomposition of NMC in the presence of carbon black was confirmed by TGA analysis of the NMC/carbon black mixture, which exhibited a rapid weight loss starting at 650°C (**Fig. 6c)**. This weight loss was not observed for pure NMC without carbon, further confirming the role of carbon black in the decomposition process. When a reductant, such as carbon, is present along with a lithium transition metal oxide, it can lower the decomposition temperature of the oxide.[43]

The onset temperature of NMC decomposition can be influenced by the presence of the PVDF binder and the carbon content in the mixture. It was found that the NMC/carbon mixture (94:6 wt.%) had a lower decomposition temperature of 650 °C, while the NMC/PVDF/carbon mixture (94:3:3 wt.%) showed a higher decomposition temperature of 700 °C.

The TGA analysis also revealed that both the PC-recovered and manually scraped-off samples exhibited two minor stages of weight loss. The first stage, occurring around 180–400°C, is attributed to the decomposition of both PVDF residue and gel-like PC-related residue. [16, 44, 4] The second stage, occurring around 400–570 °C, corresponds to the decomposition of carbon residue.[16, 45, 46] These weight losses indicate the presence of impurities, including PVDF- and carbon-related species, on the surface of both samples.

Comparing the weight loss percentages, the PC-recovered sample showed a total weight loss of 0.8 %, while the manually scraped-off sample exhibited a total weight loss of 2.1 % (0.7% of PVDF and 1.4% of carbon). This suggests that the PC-based liberation/separation process effectively reduces the number of impurities on the surface of the NMC particles. However, even after the PC-based process, the PC-recovered sample still contained carbon residues that induced a rapid weight loss starting at 700 °C. The presence of dispersed carbon among the NMC particles was confirmed with EDAX mapping (**Fig. S3**). Additionally, the PC-recovered sample showed a slight weight increase at 550–675°C, which could be attributed to buoyancy effects and oxidation of the PC-adsorbed species, although the exact cause is unclear.[47]

Electrochemical performance of the PC-recovered cathode material. The complete removal of PVDF and carbon residues from the active material can indeed be challenging due to their strong bond. These residues can have negative effects on battery performance by obstructing the Li-ion pathway in the composite electrode structure and accelerating side reactions in the battery. Any excess of residual PVDF and carbon beyond the optimized amount can lead to changes in porosity and tortuosity within the original electrode microstructure, affecting battery performance.[48-50] Furthermore, the performance and functionality of these residual species can differ from their intended purpose, potentially leading to adverse effects on battery performance. Therefore, reclaimed cathode materials, which may contain impurities such as PVDF and carbon residue, may exhibit increased resistance and capacity fade compared to their pristine counterparts.[10]

To address this issue, the PC-based process developed in this study offers a viable approach. Based on our electrochemical analyses on the PC-recovered cathode, the PC-based process can convert PVDF residues into a Li-ion conducting polymer layer by incorporating PC molecules into the PVDF polymer chains. This transformation of PVDF residues in Li-ion conducting species may help mitigate the negative impact of PVDF and carbon residues on battery performance.

The electrochemical performance of the NMC electrodes before and after the PC-based process was compared in **Fig. 7**. The charge/discharge profiles (**Fig. 7a**) of the baseline and PC-recovered cathodes were comparable to each other. Both electrodes showed a well-defined voltage plateau at approximately 3.7 V, at which Li (de)intercalation reactions occur, suggesting the lattice structure of the recovered cathode remained intact during the PC-based process. The reversible discharge capacity of the reclaimed electrode was mostly comparable to that of the baseline electrode, with a slight difference attributed to the presence of impurities on the surface of the active material. Considering no significant differences between the baseline and recovered materials in terms of their (003) peak positions and intensity ratios of the (003)/(104) peaks (**Fig. 6a**), the slight capacity difference was not associated with potential lithium loss of the recovered material during the PC-based process. ICP analysis also confirmed that there was no significant difference in the lithium ratio between the baseline and recovered materials (**Table S4**). These observations confirmed that the PC-recovered electrode retained its original capacity and did not experience a significant deterioration in its electrochemical reactivity. Interestingly, the CV charge capacity of the recovered electrode decreased after the PC-based recovery process, indicating an improvement in cell resistance with the recovered electrode. The reduction in CV charge capacity suggests that the PC-based process effectively addressed the issue of increased resistance caused by PVDF and carbon residues, leading to improved electrochemical performance of the recovered electrode.

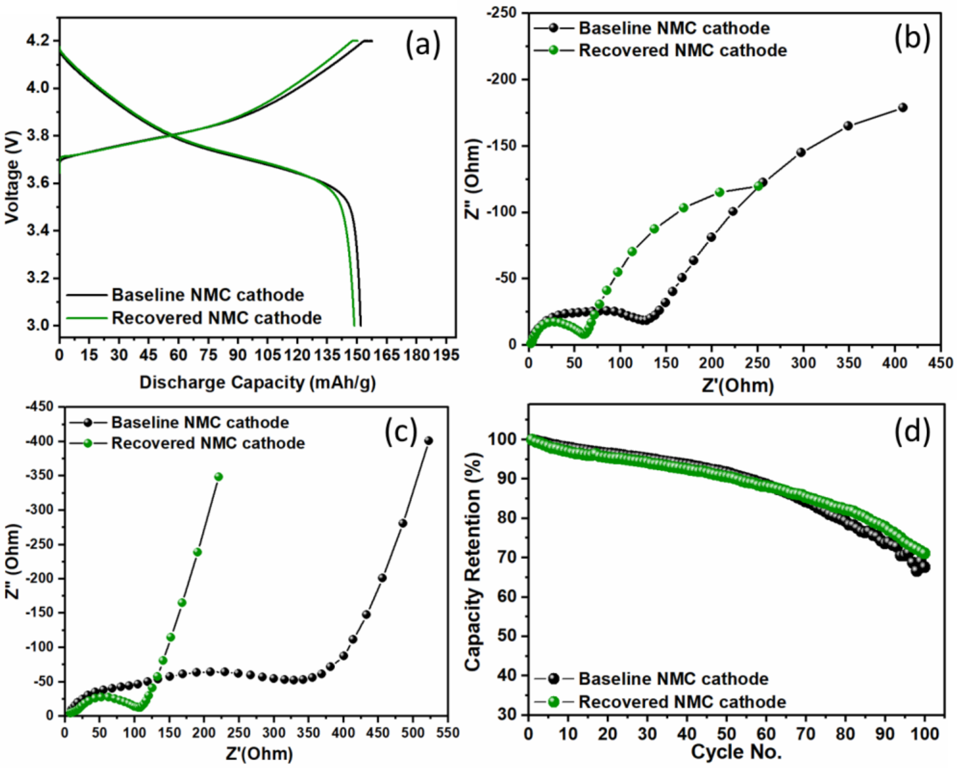


Fig. 7. Electrochemical performance of the PC-recovered cathode in comparison to those of the baseline cathode before the PC-based process: (a) Charge-discharge profiles at the end of the formation cycle (5th cycle, C/10 rate); (b) Nyquist plots after the 5th cycle and 100th cycle; (c) Comparison of cycle performance at C/3 rate.

The improved cell resistance of the recovered electrode was further confirmed by EIS results. The Nyquist plots (**Fig. 7b and 7c**) show a clear distinction between the baseline and the reclaimed NMC cathodes, particularly in the range of the high to medium frequencies, which is indicative of charge transfer resistance.[10, 42] After the initial 5 cycles (i.e., formation cycle), the charge transfer resistance of the recovered electrode decreased compared to the baseline electrode (**Fig. 7b**). Moreover, the increase in charge transfer resistance after long-term cycling (i.e., 100 cycles) was significantly lower for the PC-recovered electrode compared to the baseline electrode (**Fig. 7c**).

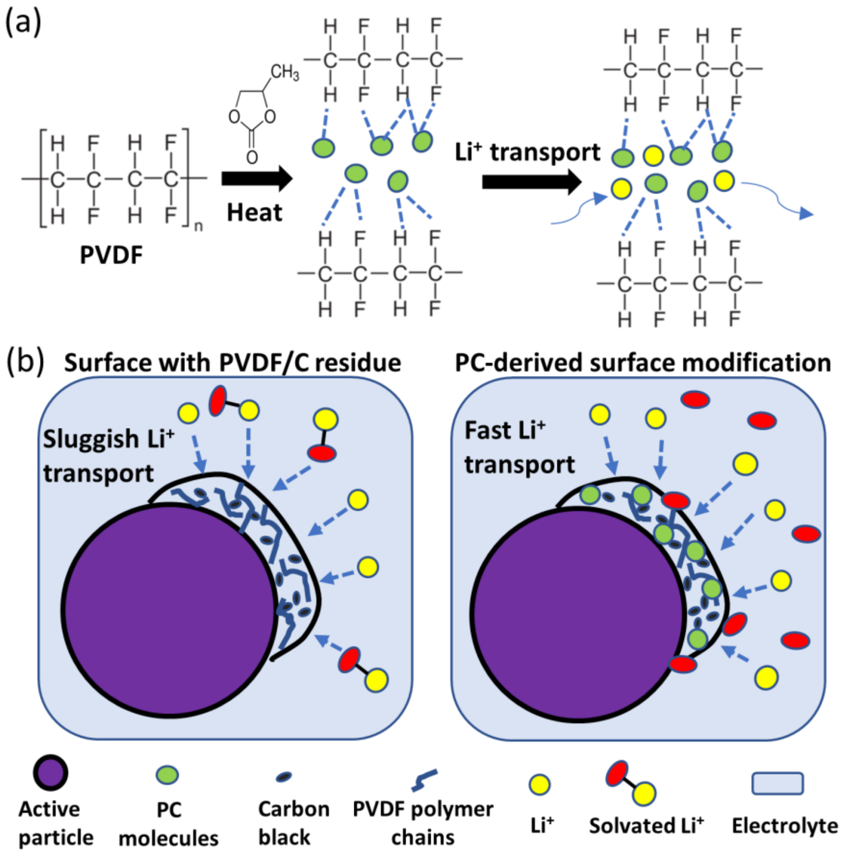


Fig. 8. Conceptual illustration of the PC-derived surface modification: (a) dissociation of solvated Li ions via PC molecules incorporated in the PVDF residue. (b) Li-ion movement through the residue polymer structure.

The reduction of charge transfer resistance observed for the recovered electrode can be associated with the improved ionic conductivity at the electrode/electrolyte interface facilitated by the plasticizer effect of PC. As illustrated in Fig. 8, the surface modification derived by PC during the PC-based liberation/separation process may be one of the possible reasons for the lower charge transfer resistance of the recovered electrode. During the process, PC molecules are incorporated into the PVDF polymer chains, some of which are trapped in the $[-CH_2-CF_2-]_n$ structure. The incorporated PC molecules not only soften the residual PVDF polymer structure, making it easier for Li ions to move, but also promote the dissociation of solvated Li ions.[40, 51] This PC-incorporated PVDF residue on the active particle can act as a Li-ion conducting layer, allowing more efficient Li-ion segmental motion through the C=O and C-F bonds with high electronegativity.[40] This explanation is based upon the Li conduction mechanism of the gel polymer electrolytes incorporating PC plasticizer.[37-41, 51] PC is widely used as a plasticizer for PVDF-based gel polymer electrolytes.[39, 41, 51, 52] Previous studies have shown that the addition of PC plasticizer can decrease the glass transition temperatures of the PVDF-based polymers as well as soften the polymer backbones, resulting in high segmental motion for Li ions. [39, 41, 51, 52] Our study also confirmed that PC can interact with PVDF and cause changes in the flexibility of the polymer chains, leading to the formation of a gel-like product (**Fig. S4a**).

Further evidence of PC incorporation into PVDF polymer can be found in FTIR analysis (**Fig. S4b**). We observed significant differences in the FTIR spectra between PC and the gel-like product (PV-PVDF). Notably, the main band at 1793 cm^{-1}, corresponding to the stretching vibration of C=O in PC, disappeared in the PC-PVDF spectrum.[53] This indicates that the stretching vibration mode of C=O in PC was strongly affected by interactions with other molecules in PVDF binder. The interactions of PC with the PVDF polymer chains can alter the vibrational properties of the carbonyl group, leading to the loss of the carbonyl peak in the FTIR spectrum. Similarly, the bands at 1184 and 1120 cm^{-1}, assigned to the antisymmetric stretching of C-O-O, were not clearly visible in the PC-PVDF spectrum.[53] Furthermore, the frequency band at 1053 cm^{-1}, corresponding to the symmetric stretching mode of C-O in PC, shifted to a lower wavenumber, 1038 cm^{-1}, for PC-PVDF.[53] These observations provide clear evidence of PC incorporation into PVDF and suggest potential hydrogen bonding interactions between the carbonyl oxygen atoms in PC and the hydrogen atoms in PVDF.

The PC-derived surface modification potentially influenced the cycle performance of the PC-recovered electrode. The capacity retention for the recovered electrode (71.0%) was slightly higher than that of the baseline electrode (67.6%) (**Fig. 7c**). This slight improvement in cycle performance can be attributed to the lower cell resistance associated with faster Li conduction at the electrode/electrolyte interface, facilitated by the PC-derived surface modification. The effectiveness of the PC-derived surface modification can be also observed from the improved rate capability of the recovered electrode compared to the baseline electrode (**Fig. S5**). The enhanced rate capability further validated the positive impact of the surface modification facilitated by the PC plasticizer effect.

Conclusions

The successful development of a non-destructive liberation/separation process for retrieving cathode active materials from spent batteries and electrode scraps is crucial for direct cathode recycling. In this study, a biodegradable green solvent, PC, was proposed as a suitable solvent for large-scale use in the liberation/separation process. The PC-based process demonstrated effective liberation and separation of the cathode active material from the battery electrode, operating at low temperature and within a short time.

The dissolution and delamination mechanisms involved in the PC-based process were discussed in detail, providing insights into how the process works. Importantly, the reclaimed cathode material retained its original crystal structure, particle morphology, chemical composition, and electrochemical performance, indicating that the developed process preserves the essential characteristics of the cathode material necessary for direct cathode recycling.

Moreover, the recovered cathode showed improved charge transfer resistance despite the presence of impurities on the surface of the active material. This improvement was attributed to the transformation of PVDF residues into a Li-ion conducting polymer layer during the PC-based process. This finding addresses the challenges of completely removing PVDF/C residues from the active particle and demonstrates the effectiveness of the PC-based process in dealing with this issue.

Future studies will focus on further improving the purity of the recovered cathode material by developing appropriate cleaning methods. This will enhance the overall effectiveness of the PC-based liberation/separation process and provide additional evidence of the benefits of PC-derived surface modification.

Overall, the developed PC-based liberation/separation process holds great promise for direct cathode recycling and is expected to attract significant attention in the battery recycling and manufacturing industries. It offers a viable and environmentally friendly solution for recovering cathode active materials and advancing the circular economy of battery materials.

Supporting Information

The Hansen and Hildebrand solubility parameters of solvents; Ni/Mn/Co composition ratio of recovered NMC (EDAX analysis); Intensity ratio of I_{003}/I_{104} of recovered NMC (XRD analysis); Atomic ratio of Li, Ni, Mn, and Co (ICP-MS analysis); Photos of dissolution of PVDF in PC at different temperatures; SEM/EDAX analysis of recovered NMC; EDAX mapping of recovered NMC; FTIR spectra of PC, PVDF, and PC-PVDF; Rate capability of the baseline and recovered cathodes.

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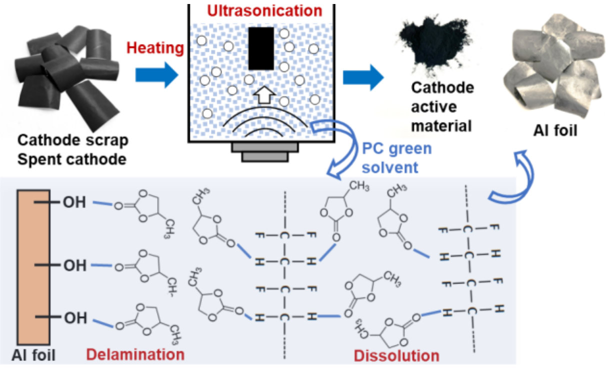

Synopsis

A biodegradable green solvent, PC, was used to liberate and separate cathode active materials from electrode scraps.

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