

# Achieving low-temperature hydrothermal relithiation by redox mediation for direct recycling of spent lithium-ion battery cathodes

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## ABSTRACT

Lithium-ion battery (LIB) recycling is an urgent need to address the massive generation of spent LIBs from portable devices and electrical vehicles. However, the large-scale recycling is hampered by economic and safety issues associated with today's recycling processes. Here, we demonstrate a safe and energy efficient direct regeneration process based on low-temperature hydrothermal relithiation (LTHR) at low pressure for spent  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$  ( $0 < x, y, z < 1$ ,  $x + y + z = 1$ , or NCM) cathode materials. A low concentration of low-cost redox mediator is employed to improve the relithiation kinetics of spent NCM materials, enabling full relithiation temperature to be reduced from 220 °C to 100 °C or below. Correspondingly, the pressure incurred in the relithiation process can be reduced from ~25 bar to 1 bar, offering significantly improved operation safety. Specifically, three NCM materials, including chemically delithiated NCM111, cycled (degraded) NCM111, and cycled NCM622, were successfully regenerated with complete recovery of composition, crystal structure, and electrochemical performance, achieving the same effectiveness as that achieved at high temperature process. Meanwhile, the total energy consumption of spent cell recycling and the greenhouse gas emission is also reduced. This work provides a facile and scalable way to more sustainable LIB recycling with high economic return, high operation safety and low cost.

## 1. Introduction

Lithium-ion batteries (LIBs) are dominant power sources for portable electronic devices and electric vehicles (EVs) because of their high energy density. With an average lifespan of 5–10 years, a massive amount of LIBs will be retired in the next several years [1,2]. It is estimated that about 1 million EV batteries will reach their end of life (EOL) by 2025, which may cause significant issues if they are not properly treated [3]. The flammable and hazardous wastes (such as electrolyte and transition metals) caused by inappropriate disposal of spent LIBs can contaminate soil, water and air [4]. As a result, developing effective and environment-friendly LIB recycling strategies has become an urgent need not only to reduce the environmental impact of LIB waste but also to recover valuable resources such lithium (Li) and cobalt (Co) and

nickel (Ni) [5].

Recently, recycling of LIB cathodes has gained majority of the interest due to the high value of Co, Ni and Li [6]. In general, there are three primary recycling methods: pyrometallurgical, hydrometallurgical, and direct recycling processes. The pyrometallurgical process is based on a high-temperature smelting process which often involves burning mixed LIB materials followed by chemical separation. This process features low operational complexity, ease of scaling up development, yet has relatively low recovery efficiency [7]. In contrast, aqueous chemistry is generally used in the hydrometallurgical processes with high recovery efficiency but complex operation procedures, which involves leaching in acids followed by precipitation, chemical separation and purification [8–11]. While pyrometallurgical and hydrometallurgical processes represent the state-of-the-art technologies in the

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recycling industry, the involvement of high-temperature smelting and extensive usage of acid and base chemicals raises concerns on high operation costs and secondary pollution, respectively [12,13]. Combining pyrometallurgy and hydrometallurgy recycling approaches has drawn great attractions to reduce the energy and reagents cost as well as increasing recovery efficiency [14]. A recent advancement in the pyrometallurgy is the closed-loop “hydro-to-cathode” approach, which eliminated the complicated chemical separation of Ni, Co and Mn, offering battery recovery efficiency and lower operation cost [15]. Nevertheless, all the above methods require complete breakdown of cathode particles (e.g., NCM) to their elemental products (e.g.,  $\text{CoSO}_4$ ,  $\text{NiSO}_4$ ,  $\text{Li}_2\text{CO}_3$ ), which loses the significant amount of embedded energy in the cathode particle structures [8]. On the other hand, the direct recycling method involves physical separation processes to harvest cathode and anode materials with mild-condition post treatment to repair the compositional and structural defects of the electrode particles, simultaneously retaining their original compound structures and the embedded energy [15,16]. A comprehensive comparison over these current recycling processes is included in Table S1. In order to achieve a high efficiency recycling with the higher economics [17], claiming more embedded energy is important to mitigate energy consumption and raw materials loss inside the entire process loop [18]. In this regard, direct recycling holds the potential to maximize the value recovered from LIBs [7].

In the past a few years, the direct LIB cathode regeneration based on hydrothermal relithiation followed by a short post annealing step has been reported by our and several other groups, which demonstrated effective reconstruction of the morphology, composition, and crystal structure of spent  $\text{LiCoO}_2$  (LCO) [17,19,20],  $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$  (NCM111) [21–24],  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  (NCM523) [21,25],  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  (NCM622) [21] and  $\text{LiFePO}_4$  (LFP) [26] cathodes, leading to the same level of electrochemical performance as their pristine materials. It is worth noting that our post sintering process for only 4 h after the hydrothermal process is much shorter than the long-term annealing for 10 h or even longer, normally used in solid state synthesis of cathodes [27–31]. This method features its simple operation and low energy consumption. It not only takes the advantage of the hydrothermal relithiation process to recover the cathode compositions without concerning the variation of Li loss in different feedstocks of degraded LIBs but also leverages the short sintering process to recover the cathode microstructure with desirable stoichiometry and crystallinity [24]. However, hydrothermal relithiation temperature higher than 200 °C (e.g., 220 °C) is generally required for full recovery of the Li deficiencies for good electrochemical properties due to the kinetic limitations of relithiation at low temperature [21,22]. Such an aqueous relithiation process could bring up potential safety concerns for large-scale operation due to the high vapor pressure (e.g., 25 bar at 220 °C) incurred inside the relithiation reactor [16]. Therefore, developing a safe and energy efficient hydrothermal relithiation process is highly desired for high-safety practical application.

Here, we significantly expanded the direct recycling capability by demonstrating a versatile low-temperature hydrothermal relithiation (LTHR) process to recover the Li composition of degraded NCM cathode materials more efficiently and safely at low pressure. The success of this general process is based on introducing a class of reducing agents as green additives (GAs) in the aqueous relithiation solution (LiOH solution) with low concentration (1%–3% v/v). These additives allow the hydrothermal relithiation temperature to be reduced from 220 °C to 100 °C or below. Correspondingly, the pressure incurred in the relithiation process can be reduced from 25 bar to 1 bar. Moreover, this LTHR process shows the same effectiveness in relithiation as that achieved at high temperature process, leading to complete regeneration of chemically delithiated NCM111, cycled NCM111 and cycled NCM622. This LTHR process can pave the way to more sustainable LIB recycling with high economic return, high operation safety and low cost.

## 2. Experimental

### 2.1. Chemically delithiated NCM111

Chemically delithiated NCM111 with ~10% of Li loss, denoted as “D-NCM111”, was made by the Materials Engineering Research Facility (MERF) at Argonne National Laboratory. Briefly, pristine NCM111 (provided by Toda America Inc.) was reacted with an aqueous solution of potassium persulfate to leach Li out. Afterwards, the leached material was washed by water, then acetonitrile, and finally dried under vacuum at the ambient condition. This delithiated NCM111 was utilized as our starting material for additive screening and was manufactured at 1 kg per batch size.

### 2.2. Electrochemically degraded NCM111 and NCM622

Commercial NCM111 cells (20Ah) were disassembled from a Honda EV. To harvest this electrochemically cycled NCM111 material (denoted as “C-NCM111”), the cathode strips were rinsed with dimethyl carbonate (DMC) to eliminate the remaining electrolyte. After drying, the cathode strips were soaked in N-Methyl-2-pyrrolidone (NMP), then sonicated for 20 min to remove the NCM powders, binder, and carbon black (CB) from the aluminum substrates. The obtained solution was centrifuged for 5 min at 3500 rpm to extract the C-NCM111 powders. The precipitation was rinsed multiple times with NMP before being collected and dried for the regeneration experiment. CB has a considerably lower density than NCM111 and could be separated during the precipitation process by gravity. The schematic diagram of the material harvesting process is demonstrated in Fig. S1. Electrochemically cycled NCM622 (C-NCM622) (Vendor A) with significant capacity degradation was separated using a similar approach and supplied by Argonne National Laboratory.

### 2.3. Direct regeneration

To perform relithiation, degraded cathode powder (chemically delithiated NCM111, and electrochemically degraded NCM111 and NCM622) was stirred in 4 M LiOH aqueous solution with addition of a 1–3% (v/v) of green additive (ethanol, hydrogen peroxide or ethylene glycol) and treated by at 90 or 100 °C for relithiation, which was followed by washing with deionized water to remove the Li salt residues. After drying, the relithiated powders were mixed with 5 mol% of excessive  $\text{Li}_2\text{CO}_3$  (to compensate for the Li loss during the post-annealing process) and annealed in oxygen at 850 °C for 4 h with a ramping rate of 5 °C min<sup>−1</sup> [19,21,22].

### 2.4. Materials characterization

The chemical composition of various cathode powders was evaluated by inductively coupled plasma mass spectrometry (ICP–MS, Thermo Scientific, iCAP RQ model). The products of ethanol and ethylene glycol after hydrothermal relithiation were analyzed by a Bruker Avance III 600MHz Nuclear Magnetic Resonance (NMR) spectrometer. The surface composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS). PHI 5000 VersaProbe II system (Physical Electronics) with Al K $\alpha$  radiation (1486.6 eV) was used to collect the XPS data. X-ray powder diffraction (XRD) utilizing Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ , Bruker D2 Phaser) was used to determine the crystal structure. General Structure Analysis System (GSAS) software with the EXPGUI interface was used to perform Rietveld refinement against XRD results. A scanning electron microscope (SEM, FEI XL30) was used to examine the surface structure and morphology of various cathode particles.

### 2.5. Electrochemical characterization

The electrochemical performance of different NCM samples was

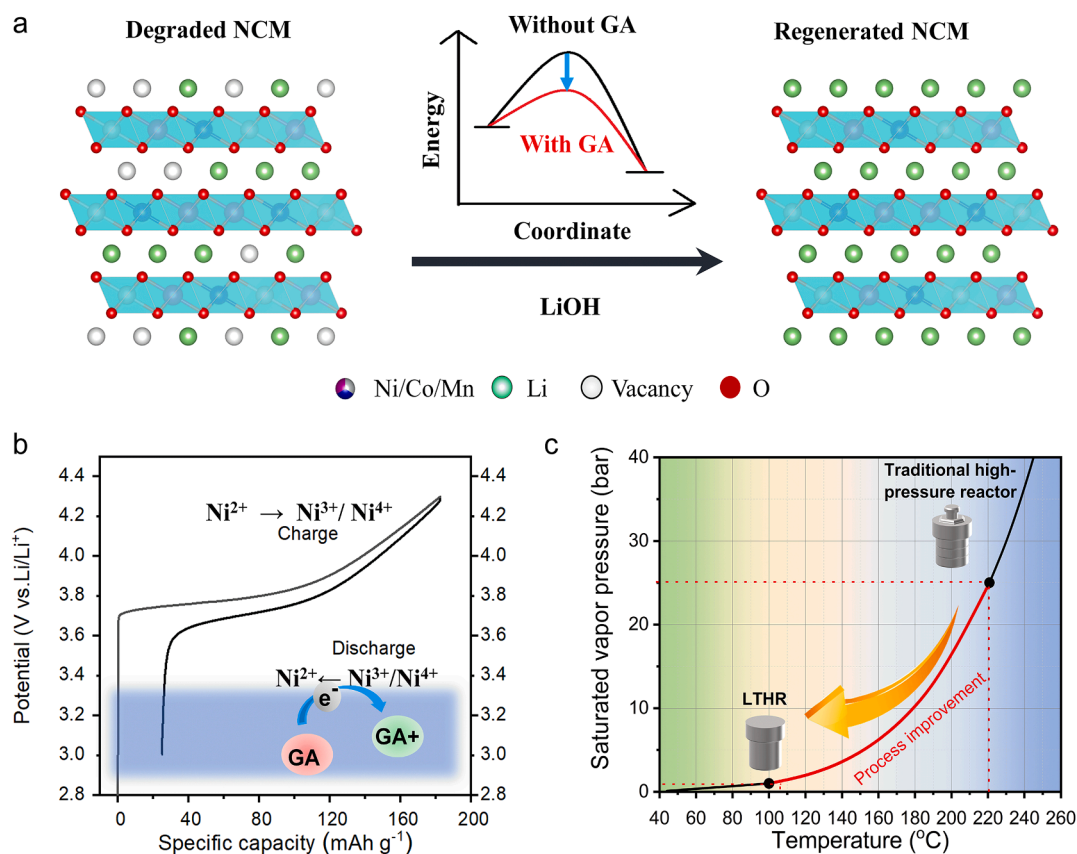
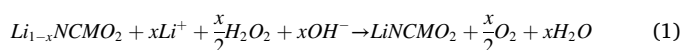
assessed by coin cells: half-cell with cathode mass loading of  $\sim 3 \text{ mg cm}^{-2}$  and  $\sim 10 \text{ mg cm}^{-2}$  and full cell with cathode mass loading of  $\sim 10 \text{ mg cm}^{-2}$ . To prepare slurries of cathode electrodes, the pristine, degraded, or regenerated NCM cathode material was mixed with conductive agent (Super P65), and polyvinylidene fluoride (PVDF) binder in a mass ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP) solvent. To prepare slurry of graphite, graphite, super P, and PVDF were mixed in a mass ratio of 90:5:5 in NMP solvent. Afterwards, the slurries were casted onto aluminum foil (cathode) and copper foil (anode) with a doctor blade before drying at  $120^\circ\text{C}$  for 12 h in a vacuum oven. The dry laminate was cut in disc-shape and calendared. Coin cells were fabricated inside a glovebox. For half-cell, a Li metal disc (thickness 1.1 mm) was used as the counter electrode and for full-cell, graphite electrode was used as the counter electrode (N/P ratio:  $\sim 1.1$ ). LP40 (1M  $\text{LiPF}_6$  in ethylene carbonate/diethyl carbonate=50:50 (v/v)) or Gen2 (1.2 M  $\text{LiPF}_6$  in EC/EMC = 3:7) was used as the electrolyte, and a tri-layer membrane (Celgard 2320) was used as the separator. Galvanostatic charge-discharge was tested using a Neware battery cycler in the potential range of 3.0–4.3 V for half-cell and 2.8V–4.2V for full cell at room temperatures with 4 activation cycles at the rate of C/10 followed by long cycles at a constant rate of C/3 or 1 C.

### 3. Results and discussion

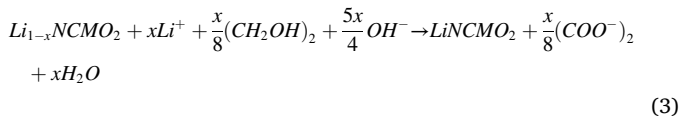
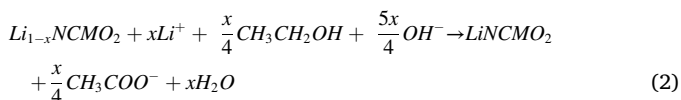
#### 3.1. The LTHR process for degraded NCM111

An overview of the LTHR relithiation process for NCM111 is illustrated in Fig. 1. To demonstrate the effectiveness of our LTHR process by redox mediation for direct recycling, the degraded NCM111 particles were treated via relithiation in LiOH solution with the addition of different green reducing agents (GAs). In this process, the key to

regenerate the degraded NCM111 effectively at low temperature is to reduce the  $\text{Ni}^{3+}$  ions in the degraded NCM111 into  $\text{Ni}^{2+}$  ions and to compensate for the Li deficiency in the structure for charge balance. We proposed that a reductive environment can help lower the activation barrier, which can facilitate  $\text{Ni}^{3+}$  reduction (Fig. 1a). In order to validate this, here, we tested the solution treatment method with the GAs to promote the redox reaction, in which  $\text{Ni}^{3+}$  ions in the crystal can be more easily reduced due to the donation of electrons from the reducing agents. Consequently, the facile reduction of  $\text{Ni}^{3+}$  would promote the insertion of  $\text{Li}^+$  from the solution into the cathode material, sharing the same essence of electrochemical  $\text{Li}^+$  insertion (Fig. 1b). Three different GAs were tested to verify this mechanism. They have a standard reduction potential of  $-0.77 \text{ V}$  (ethanol, versus standard hydrogen electrode or SHE) [32],  $0.15 \text{ V}$  (hydrogen peroxide) [33], and  $-0.72 \text{ V}$  (ethylene glycol) [32], respectively, which are all below the  $\text{Ni}^{3+}/\text{Ni}^{2+}$  redox potential ( $\sim 0.7 \text{ V}$ ). The Gibbs free energies,  $\Delta G = -nFE = -nF(0.7 - E_{\text{GA}})$ , of the reaction between NMC materials and GAs are negative, which indicates the relithiation of degraded NCM materials with GAs are thermodynamically favorable. To detect the oxidized products of the three reducing agents in 4 M LiOH solution after hydrothermal process, NMR spectra were measured, which showed that the oxidized products of ethanol, hydrogen peroxide and ethylene glycol in 4 M LiOH solution are lithium acetate [32,34], oxygen [33], and lithium oxalate [32,34] (Fig. S2), respectively, with the following reactions occur:



**Fig. 1. Overview of the relithiation process of degraded NCM111.** (a) Schematic illustration of hydrothermal relithiation-based direct regeneration process of degraded NCM materials, (b) illustration the role of GAs in LTHR process, and (c) the saturation vapor pressure of water under various temperatures associated with equipment changes from traditional high-pressure reactor at  $220^\circ\text{C}$  and low-pressure reactor for LTHR process at  $100^\circ\text{C}$  [35].



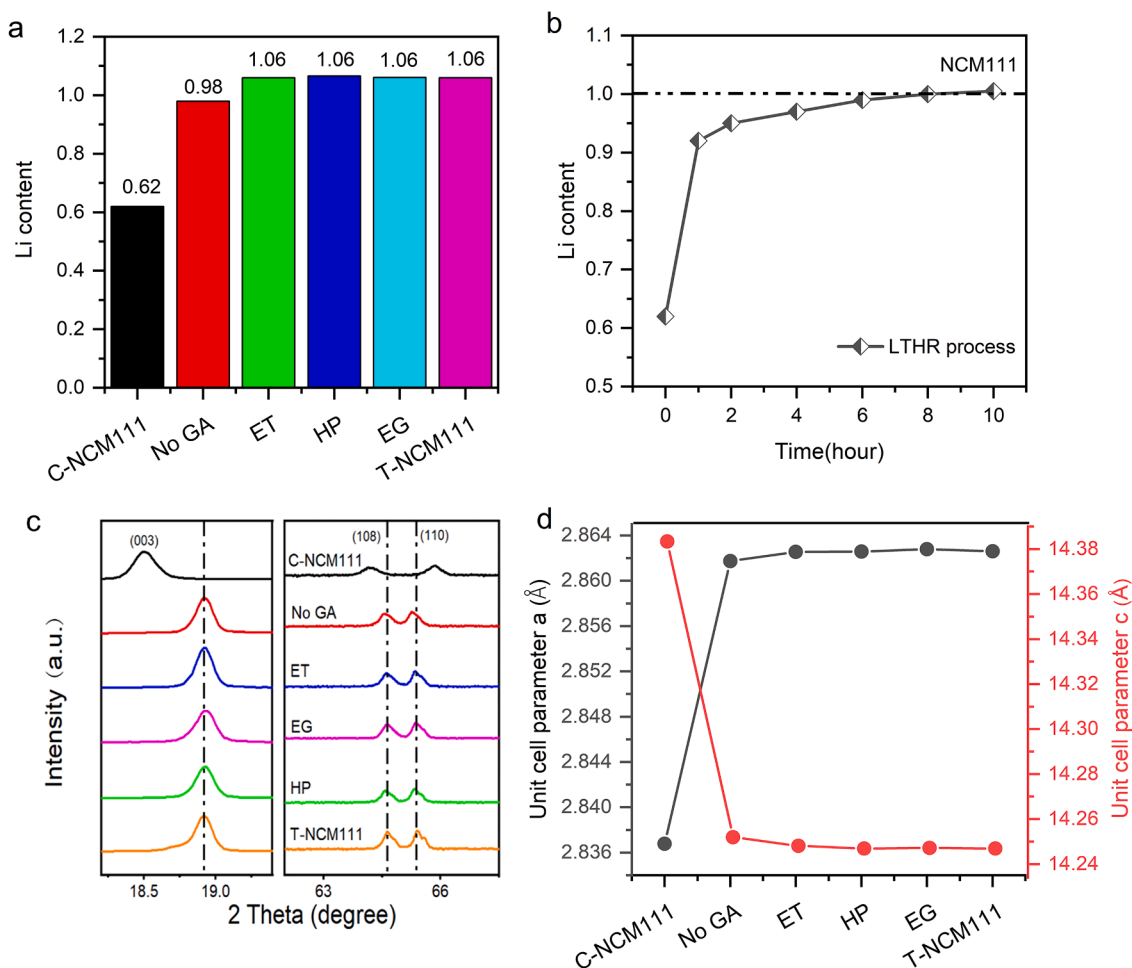
These additives thus allow the relithiation to proceed at a relatively low temperature and pressure due to improved redox kinetics, lowering the energy costs, and improving the operating safety (Fig. 1c). Although all three GAs could assist to regenerate NMCs, EG is the most suitable one among them for the practical application due to its low cost and safety concerns (Table S2). Hence, in the following study we evaluated three GAs but mainly employed EG as a reducing agent to study the mechanism of LTHR process.

### 3.2. Composition and structure recovery via the LTHR-based regeneration

To further evaluate the effectiveness of our LTHR method, two types of degraded NCM111 particles were initially used to study the impact of redox mediation. One is the D-NCM111 with 10% of Li loss, which is the model material from the ReCell project [22], and the other one is the C-NCM111 from a Honda EV (Fig. S1). Initial screening of GAs was conducted using D-NCM111 and then systematic kinetics study was

performed on C-NCM111. Specifically, C-NCM111 was subject to relithiation in a LiOH solution at 100 °C for 8 h with assistance of three different GAs, including ethanol (ET), ethylene glycol (EG) and hydrogen peroxide (HP) followed by short annealing at 850 °C. As a further validation of the crucial role of reducing agent, the C-NCM111 was treated with a LiOH solution without the reducing agent under the same conditions. An illustration of the whole process is shown in Fig. S3. It is noted that transition metal leaching indeed exists during prolonged cycling, especially in harsh conditions for spent cathodes. The extent of leaching is affected by cycling conditions (temperature, upper cutoff voltage, etc.) [36], microstructures of cathodes [37], cathode material types (especially Mn-rich) [38], and so on. However, transition metal leaching is not a significant issue in this case for NCMs. Based on the ICP results, no obvious transition metal composition changes and dissolution of transition metal ions was found in the spent NCMs compared with comparable pristine materials (Table S3). The leaching amount for transition metal is minimal and transition metal leaching issue is insignificant in our case. To fully demonstrate the viability of direct recycling, spent cells from a variety of application scenarios need to be tested.

ICP-MS test was carried out to determine the Li content (a molar ratio between Li and transition metals) of each sample. To note that, ICP-MS tests for each sample were usually repeatedly tested for three times and consistent results are obtained (Table S4). As shown by the ICP-MS results (Fig. 2a), the Li content ( $x_{\text{Li}}$ ) of C-NCM111 ( $x_{\text{Li}} = 0.62$ ) was successfully recovered after the regeneration process with GAs at 100 °C



**Fig. 2. Relithiation kinetics.** (a) Li content in different NCM111 particles with and without relithiation obtained by ICP results, (b) composition evolution of cycled NCM111 during relithiation via LTHR process, (c) XRD patterns of cathode samples relithiated at 100 °C with three different GAs (ET, EG and HP) as well as control samples (T-NCM111), (d) unit cell parameters of a and c of different NCM111 samples.



( $x_{\text{Li}} = 1.06$ ), which maintained the same stoichiometry as T-NCM111 ( $x_{\text{Li}} = 1.06$ ). All of the three GAs exhibited almost the same effect on the composition recovery. In contrast, the Li content can only achieve 0.98 under the same condition with the absence of GA. This effect was also observed in the D-NCM111 case, where the Li content recovered from 0.9 to 1.06 with GAs (Table S3). Furthermore, we evaluated the relithiation kinetics for composition recovery of the LTHR process (Fig. 2b). With assistance of the GA, an 8h-LTHR process is sufficient to achieve a 100% composition recovery as the 220 °C process does [21].

The morphology of the regenerated samples as well as the control sample was further compared. The LTHR process exhibited no influence on the particle morphology (Figs. S4 and S5), attributed to the mild regeneration conditions. XRD results also confirm the effectiveness of the LTHR process on the crystal structure recovery of the C-NCM111 and D-NCM111 samples (Figs. 2c, d and S6). Overall, the diffraction peaks of all the samples matched well with the typical  $\alpha$ -NaFeO<sub>2</sub> structure with the  $R\bar{3}m$  space group, indicating that the bulk structure of the NCM111 was not affected by electrochemical cycling (C-NCM111), chemical delithiation (D-NCM111) and our regeneration strategy, which again demonstrated the viability of the LTHR-based direct regeneration process.

Nevertheless, microstructure evolution was observed clearly during the entire regeneration process. C-NCM111 exhibits a (003) peak shift to

a lower degree (Fig. 2d), which can be explained by the increased electrostatic repulsion between the oxygen layers along the  $c$  direction when  $\text{Li}^+$  is deficient [19,39]. Meanwhile, the spacing between the peaks in the (108)/(110) doublets increases, indicating the decrease in  $a$  lattice parameters due to the decrease in average metal–metal distance caused by smaller effective ionic radii of  $\text{Ni}^{3+}$  compared with  $\text{Ni}^{2+}$  [40]. Similar peak shifting can be also observed in D-NCM111 (Fig. S6). The lattice parameters of  $a$  and  $c$  unit cell were determined via Rietveld refinement (Table S3). The  $a$  lattice parameter decreased from 2.860 Å (T-NCM111) to 2.837 Å (C-NCM111) and 2.848 Å (D-NCM111), respectively. The  $c$  lattice parameter increased from 14.247 Å (T-NCM111) to 14.383 Å (C-NCM111) and 14.311 Å (D-NCM111), respectively, which is consistent with the peak shift from the XRD results. After the LTHR process, the (003), (108), and (110) peaks obviously shifted back to the original position as in the pristine T-NCM111, indicating the recovery of the original microstructure (Figs. 2d and S6b). The lattice parameters of the  $a$  and  $c$  of the regenerated samples were close to those of the T-NCM111, indicating that  $\text{Li}^+$  ions reached their equilibrium state in the lattice structure despite the low relithiation temperature. Furthermore, the Li/Ni mixing ratio of C-NCM111 decreased from 5.47 to 2.40 (ET), 2.43 (HP), and 2.41 (EG), respectively (Table S3), reaching the mixing ratio nearly the same as the pristine T-NCM111 (2.39). In contrast, the Li/Ni mixing ratio did not perfectly

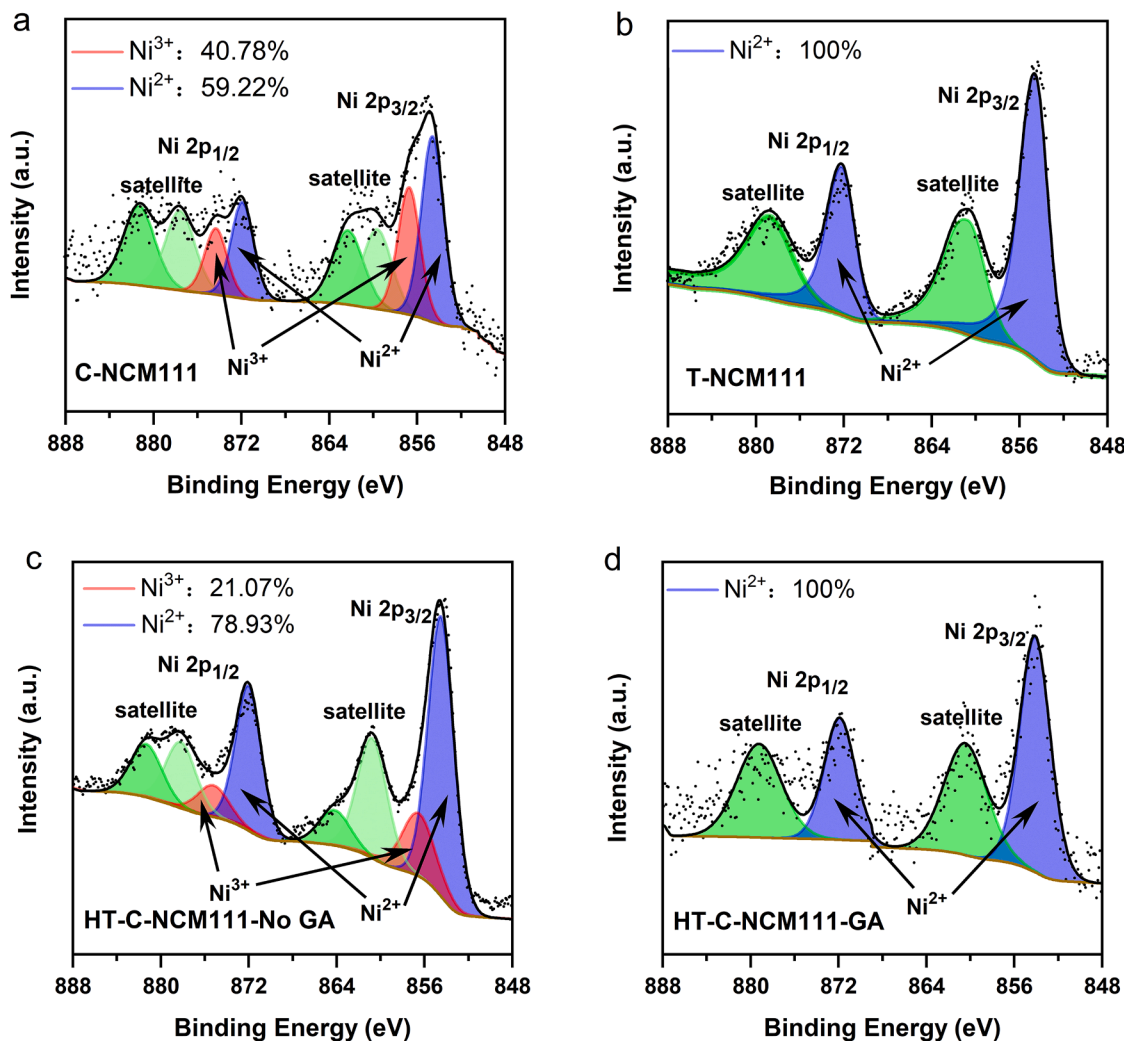


Fig. 3. XPS spectra in Ni 2p region of different NCM111 samples. (a) C-NCM111, (b) T-NCM111, and relithiated C-NCM111 without GA (c) and (d) with GA at 100 °C.

recover to the original condition without GA, which redemonstrates that GA is conducive to regenerating NCM111 in the LTHR process.

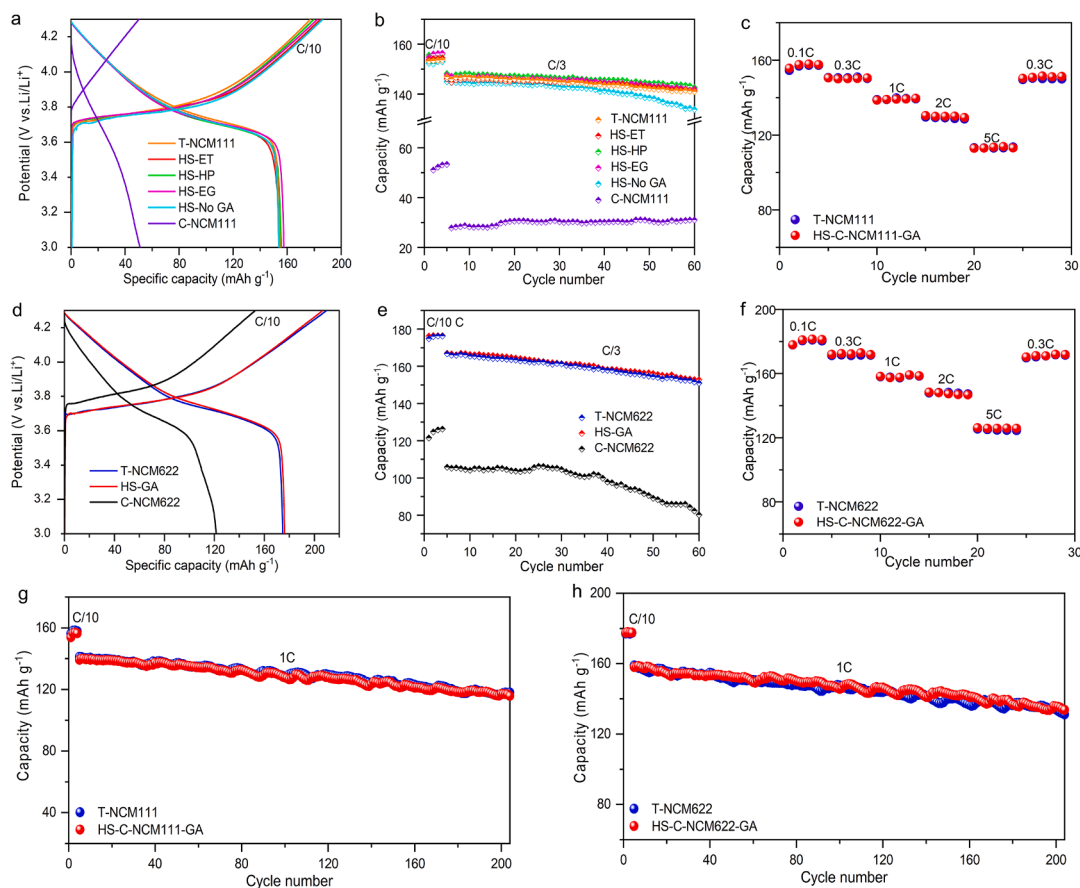
### 3.3. Surface composition study

To further understand the role of GA in the LTHR process, XPS measurement was performed to determine the valence state of Ni in different NCM111 before annealing (Fig. 3). Due to the lower redox voltage of  $\text{Ni}^{3+}/\text{Ni}^{2+}$ , only the variation of Ni valence status is expected to occur as the maximum Li deficiency is only 0.4 in this case [22,41] 40.78% of Ni was observed in the form of  $\text{Ni}^{3+}$  in the C-NCM111 as shown in Fig. 3a. After relithiation in the blank LiOH solution, ~21.07% of Ni remained at  $\text{Ni}^{3+}$  while nearly 100% of  $\text{Ni}^{3+}$  was reduced to  $\text{Ni}^{2+}$  with the presence of GA [22]. In this case,  $\text{H}_2\text{O}$  serves as a weak reducing agent to reduce  $\text{Ni}^{3+}$  into  $\text{Ni}^{2+}$  [42]. In contrast, all the  $\text{Ni}^{3+}$  was reduced to  $\text{Ni}^{2+}$  via the LTHR process in the presence of a GA, suggesting the dramatically improved relithiation kinetics. Similar phenomenon was also observed for D-NCM111, where relithiation in the GA-containing LiOH solution is more effective than the one without GA (Fig. S7). Specifically, 24.68% of  $\text{Ni}^{2+}$  was converted to  $\text{Ni}^{3+}$  due to chemical delithiation. After LTHR treatment without GA, there are still 22.79% Ni remaining at  $\text{Ni}^{3+}$ , which means only 1.89% of  $\text{Ni}^{3+}$  was spontaneously reduced back to  $\text{Ni}^{2+}$  at low temperature. These results confirm the importance of GA in facilitating the reduction of  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$ , which further promotes the insertion of  $\text{Li}^+$  from the solution back into the

Li-deficient sites in the NCM cathodes to compensate for the charge.

### 3.4. Electrochemical performance of the relithiated NMC via LTHR

The electrochemical performance of C-NCM111 regenerated with the LTHR process followed by short annealing at 850 °C (denoted as “HS-C-NCM111”) was evaluated via half-cell test (Fig. 4a, b). The C-NCM111 exhibited an initial capacity of 51  $\text{mAh g}^{-1}$  due to significant Li loss (38%) and crystal structure degradation. As the effective ionic radii of  $\text{Ni}^{3+}$  is smaller than  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$  more easily occupies the Li sites when Li is in deficiency state and the cation mixing ratio increases accordingly. High cation mixing will block the  $\text{Li}^+$  transport, which reduces and  $\text{Li}^+$  storage capacity and rate performance [21]. After regeneration, all the regenerated samples and the pristine sample exhibited a similar initial discharge capacity of ~155  $\text{mAh g}^{-1}$  at C/10 in Gen2 electrolyte. The C-NCM111 treated without GA only showed 92% capacity retention at C/3 after 60 cycles. By comparison, the regenerated NCM111 with different GAs from the LTHR process all held a similar capacity retention of ~96% at C/3 after 60 cycles, which shows the same cycling stability as the pristine T-NCM111. Similar trend was also observed in the D-NCM111 samples with LP40 in half-cells (Fig. S8). The D-NCM111 exhibited an initial capacity of 134.0  $\text{mAh g}^{-1}$  at C/10 and held a capacity retention of 78% at C/3 after 50 cycles. After LTHR followed by short annealing, the initial capacity of HS-D-NCM111-GA reached 154  $\text{mAh g}^{-1}$  at C/10 and the capacity retention was improved to 91% at C/3



**Fig. 4.** Electrochemical performance of the HS-C-NCM111 and HS-C-NCM622 using EG as the reducing agent. (a) Voltage profiles and (b) cycling stability of regenerated NCM111 samples using different GAs at 100 °C and their comparison with the pristine and non-treated C-NCM111. (c) Rate performance of the regenerated NCM111 samples and the pristine NCM111. (d) Voltage profiles and (e) cycling stability of regenerated NCM622 and comparison with the pristine and non-treated C-NCM622. (f) Rate performance of the regenerated NCM622 and the pristine NCM622. Long-term cycling stability of (g) regenerated NCM111 samples as well as the pristine NCM111 and (h) regenerated NCM622 as well as the pristine NCM622 cycled at 1 C for 200 cycles.

after 50 cycles, which is on par with the pristine T-NCM111. Here, half-cell tests were evaluated under a high loading of  $10 \text{ mg/cm}^2$ . In this condition, the cycling performance was limited by the poor stability of lithium metal anode. In order to exhibit the electrochemical performance of regenerated NCM111, we evaluated rate performance and half-cell performance (at 1 C for 200 cycles) of HS-C-NCM111-GA (with EG) with a cathode loading of  $3 \text{ mg/cm}^2$  (Fig. 4c, g). The HS-C-NCM111-GA could deliver a capacity of  $141 \text{ mAh g}^{-1}$  at 1 C with 83% capacity retention after 200 cycles, similar to that of the pristine T-NCM111. The HS-C-NCM111-GA could deliver a capacity of  $157 \text{ mAh g}^{-1}$ ,  $151 \text{ mAh g}^{-1}$ ,  $140 \text{ mAh g}^{-1}$ ,  $130 \text{ mAh g}^{-1}$ ,  $113 \text{ mAh g}^{-1}$  at 0.1 C, 0.3 C, 1 C, 3 C, 5 C, respectively. The capacity of the pristine T-NCM111 could reach  $156 \text{ mAh g}^{-1}$ ,  $151 \text{ mAh g}^{-1}$ ,  $140 \text{ mAh g}^{-1}$ ,  $129 \text{ mAh g}^{-1}$ ,  $113 \text{ mAh g}^{-1}$  at 0.1 C, 0.3 C, 1 C, 3 C, 5 C, respectively. This indicates the rate capability of regenerated NCM111 has been recovered. Meanwhile, we did the full-cell test of HS-C-NCM111-GA (cathode loading:  $10 \text{ mg/cm}^2$ ) paired with graphite anode (Fig. S9a). The HS-C-NCM111-GA showed an initial capacity of  $138 \text{ mAh g}^{-1}$  at 1 C and maintained capacity of  $120 \text{ mAh g}^{-1}$  after 100 cycles in the full cell test, which is comparable with that of the pristine T-NCM111 under the same condition. The HS-C-NCM111-GA could achieve the same electrochemical performances as those of T-NCM111 in the rate, half-cell, and full-cell test, which confirmed the success of our regeneration method.

In addition, the delithiated NCM111 regenerated with the LTHR process at  $90^\circ\text{C}$  and  $100^\circ\text{C}$  followed by short annealing was denoted as ‘HS-D-NCM111-GA- $90^\circ\text{C}$ ’ and ‘HS-D-NCM111-GA- $100^\circ\text{C}$ ’ (Fig. S10), respectively. The initial capacities of HS-D-NCM111-GA- $90^\circ\text{C}$  reached  $154.0 \text{ mAh g}^{-1}$  at C/10, achieving the same level of capacity for pristine NCM111. Furthermore, the HS-D-NCM111-GA- $90^\circ\text{C}$  delivered initial capacities of  $149.8 \text{ mAh g}^{-1}$  at C/3 and the capacity retention can reach 91% after 50 cycles, which is on par with the pristine level (T-NCM111). This result indicates that the samples were effectively recovered after hydrothermal treatment at  $100^\circ\text{C}$  or even lower temperature followed by annealing.

Due to the growing interest in the high Ni NCM cathodes, our test was also extended to NCM622 by comparing the electrochemical properties between the cycled (C-NCM622), LTHR regenerated (denoted as HS-C-NCM622) and the pristine samples using Gen2 electrolyte (Fig. 4d, e). Although three GAs all worked well to regenerate NCM111, EG is the most suitable one for the practical application due to its low cost and safety concerns (Table S2). Hence, in the following study we mainly employed EG as a reducing agent to regenerate NCM622 with the LTHR process. The C-NCM622 exhibited an initial capacity of  $121 \text{ mAh g}^{-1}$  at C/10 and showed a capacity retention of 76% at C/3 after 60 cycles. With the LTHR process and short annealing, the initial capacity of HS-C-NCM622 reached  $175 \text{ mAh g}^{-1}$  at C/10 and the capacity retention of was improved to 92% at C/3 after 60 cycles, which is equal to the pristine T-NCM622. In order to show the electrochemical performance of the regenerated NCM622, we evaluated the rate performance and cycling stability in half-cells (at 1 C for 200 cycles) of HS-C-NCM622-GA (regenerated with EG as GA) with a cathode loading of  $3 \text{ mg/cm}^2$  (Fig. 4f, h). The HS-C-NCM622-GA could deliver similar rate capability and long cycling stability as that of T-NCM622. Meanwhile, we did the full-cell test of HS-C-NCM622-GA (cathode loading:  $10 \text{ mg/cm}^2$ ) paired with graphite anode (Fig. S9b). The HS-C-NCM622-GA showed a capacity of  $154 \text{ mAh g}^{-1}$  at 1 C in the first cycle and maintained capacity of  $130 \text{ mAh g}^{-1}$  after 100 cycles at 1 C in the full-cell test, which is close to that of the pristine T-NCM111 under the same condition. In summary, the HS-C-NCM622-GA could achieve the same electrochemical performances as those of T-NCM622 in the rate, half-cell, and full-cell test, which confirmed the success of NCM622 regeneration. The successful regeneration of both NCM111 and NCM622 using different GAs suggests the high efficiency and versatility of our LTHR-based direct recycling approach. All these results support our hypothesis that a reductive environment can help lower the activation barrier for  $\text{Ni}^{3+}$  reduction and relithiation, which has also been validated in related studies for LFP

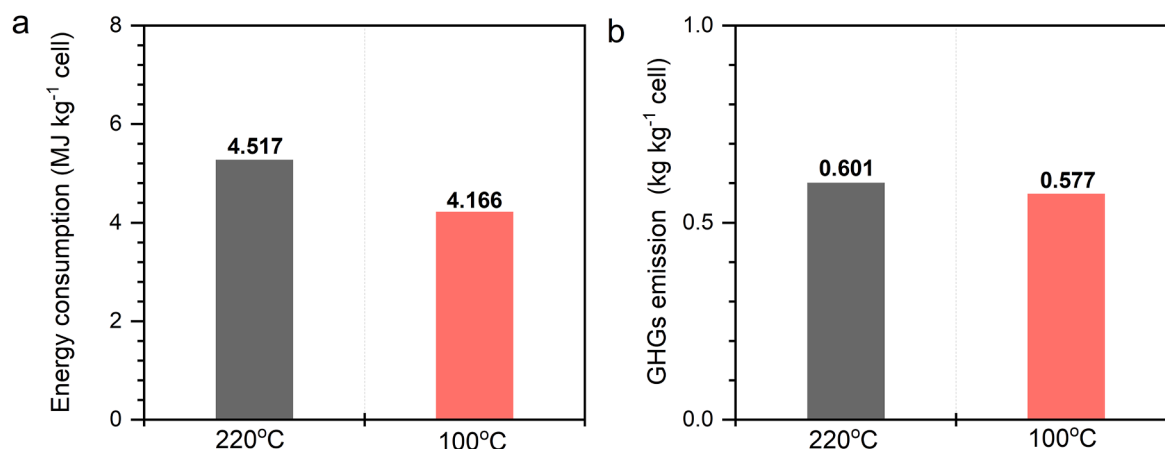
as Xu et al. reported [26,43].

To examine the difference of structural stability between regenerated materials and pristine materials, the HS-EG, HS-No GA and T-NCM111 electrodes after cycles (denoted as ‘Cycled HS-EG’, ‘Cycled HS-No GA’ and ‘Cycled T-NCM111’, respectively) were characterized by XRD (Fig. S11). The XRD diffraction peaks of all these samples still matched well with the typical layered structure without noticeable impurity phase, indicating that the bulk structure of the pristine and regenerated NCM111 were not affected by either electrochemical cycling or the recycling processing. No obvious differences in terms of crystal structure were observed between Cycled HS-EG and Cycled T-NCM111, which also demonstrates the viability of the LTHR-based direct regeneration process. However, as discussed earlier, without GA addition, Li content, Li/Ni mixing ratio, transition metal valence, and the electrochemical stability of the regenerated materials cannot perfectly recover to the original condition. After cycling, the (003) peak of Cycled HS-No GA shifts to a lower degree compared with Cycled HS-EG and Cycled T-NCM111, due to more severe Li deficiency as well as more significant lattice expansion along the *c*-axis. All these results indicates that GA is vital to regenerating NCM111 in the LTHR process to recover the composition and structure in the direct recycling process.

### 3.5. Life cycle analysis of the LTHR-based direct recycling process

For a typical hydrothermal relithiation process, NCM materials require high-pressure reactors (generally autoclaves) to hold pressure greater than 25 bar (saturation pressure of water) at  $220^\circ\text{C}$  (Fig. 1c) [16]. Due to the facilitated relithiation kinetics enabled by GAs, the LTHR can be conducted at temperatures equate to or below the boiling point of water as shown above, which allows the relithiation process to be conducted at low pressure, alleviating the necessity of high-pressure reactors [6,26]. To be more specific, when the relithiation temperature is reduced to  $100^\circ\text{C}$ , the pressure required for the LTHR process can be reduced to around 1 bar. By replacing the traditional high-pressure reactors with low cost vessels, large scale direct regeneration will be more viable for industry application without additional safety precautions compared to the previous processes [21,22].

An evaluation of the environmental and economic impact of the LTHR-based direct regeneration was conducted using the EverBatt model developed by Argonne National Laboratory using a throughput of 10,000 tons of spent LIBs per year [44]. The detailed description of methodology can be found in the supporting information. The life-cycle analysis (LCA) of the entire direct recycling process with LTHR and the traditional high-pressure reaction were performed in terms of energy consumption, greenhouse gas (GHG) emission, operation cost, and overall profit (Figs. 5 and S12). The direct recycling process is modeled by a flowchart in Fig. S13 with specific unit operations for reaction and separation. By assuming the same pretreatment and post-separation, the modeling results show that the total energy consumption was reduced from  $4.517 \text{ MJ kg}^{-1}$  of spent cells for traditional high-pressure regeneration reaction to only  $4.166 \text{ MJ kg}^{-1}$  of spent cells for LTHR (Fig. 5a). Consistently, our LTHR for direct regeneration process can also reduce around  $0.03 \text{ kg}$  of GHG emission per  $\text{kg}$  cell compared to the traditional high-pressure regeneration reaction at  $220^\circ\text{C}$  (Fig. 5b). Apart from the energy consumption and GHG emissions, the cost and profit of both processes were also modeled with the results compared in Fig. S12. Due to the reduced temperature of the relithiation process, low-grade industry waste heat can be potentially utilized to offer heat to the LTHR process. The total process cost of the direct recycling of NCM batteries was estimated to be  $\$2.07$  and  $\$2.25$  of spent battery cells processed at  $100^\circ\text{C}$  and  $220^\circ\text{C}$ , respectively. Thus, the regenerated cathode production with LTHR promises to offer additional  $\$0.18$  profit per  $\text{kg}$  of spent cells. In addition, a great amount of cost to provide safety cautions can be eliminated. As the result of the significant reductions in total energy use, GHG emissions, and processing cost, the LTHR-based direct regeneration method may be a preferable option for closed-loop, safe



**Fig. 5.** Life cycle analysis of the LTHR-based direct recycling method. (a) Energy consumption and (b) GHGs emission of our direct recycling methods based on relithiation at different temperatures.

#### LIB recycling.

In addition, our LTHR-based direct recycling method for NCMs recycling was also compared with traditional pyrometallurgical and hydrometallurgical recycling processes with LCA. The energy consumption for pyrometallurgical and hydrometallurgical recycling processes of spent NCM cells are 18.497 MJ kg<sup>-1</sup> and 30.710 MJ kg<sup>-1</sup>, respectively, which are significantly higher than the LTHR-based direct recycling process of only 4.166 MJ kg<sup>-1</sup> (Fig. S14a). As shown in Fig. S14b, for 1 kg of spent NCM cells, pyrometallurgy (2.457 kg) and hydrometallurgy (2.258 kg) released notably higher GHG than that of direct recycling method (0.577 kg). These can be explained by the high temperature smelting in the pyrometallurgical process and production of extensive chemicals used in hydrometallurgical recycling processes [22]. In addition, cost and profits related to three recycling processes are also modeled and analyzed shown in Figs. S14c and S14d. The total costs for pyrometallurgical, hydrometallurgical and LTHR-based direct recycling of 1 kg of spent NCM cells are \$3.10, \$2.54, and \$2.04, respectively. This is due to the expensive equipment, extensive usage of chemicals and high energy consumption of pyrometallurgical and hydrometallurgical recycling process. As Ni and Co represent most of the valuable of cathodes, profits of \$2.16 and \$3.07 through pyrometallurgical and hydrometallurgical recycling of 1 kg spent NCM cells can still be earned, respectively, which are still far lower than the profit for LTHR process (\$4.85). Overall, discussions above highlight potential economic and environmental benefits of our LTHR-based direct recycling method.

Although the EverBatt model might have oversimplified the actual LIB recycling process, we believe a side-by-side comparison of these recycling approaches will provide useful insights into the next-generation LIB recycling strategies. All the above analysis together shows this LTHR-based direct recycling method stands to benefit from a "4H" approach for batteries recycling, which has the objectives of high efficiency, high economic return, high environmental benefit and high safety [45], representing a new trend in sustainable LIB recycling. Finally, it is worth mentioning that there are both opportunities and challenges with scaling up the regeneration process from lab scale to industry scale. For example, we employed organic solvents, DMC and NMP, to separate and wash cycled NCM powders from spent cells for relatively small scale (*i.e.*, 1–100 g) in this work. However, industry usually employs solvent-free mechanical separation technology instead of organic solvents. About the challenges, impurities, such as Cu [46], Fe [47] and Al [48] as well as polymer binder and residual carbons, will have influence on the electrochemical performance of regenerated cathode materials, which needs systematic investigation. Further development of in-depth investigation and optimization of battery

handling, and materials separation will pave the way for adoption of the direct recycling method in the industry.

#### 4. Conclusions

In summary, we successfully demonstrated an efficient, safe, and environmentally friendly direct cycling method based on a LTHR process at or below 100 °C. Three different NCM materials, including C-NCM111, D-NCM111, and C-NCM622, were successfully regenerated using the LTHR process. With a small amount of GAs in the aqueous Li solution, relithiation reaction at 100 °C is sufficient to achieve a complete recovery of composition, crystal structure, and electrochemical performance for heavily degraded NCM cathode materials. Compared with the previous direct regeneration process that relies on high temperature relithiation (*e.g.*, 220 °C), the LTHR process further reduces the energy consumption, GHGs emission and safety concerns during LIBs recycling process, providing a facile and scalable approach to move LIB direct recycling closer to practical applications.

#### CRediT authorship contribution statement

**Xiaolu Yu:** Investigation, Methodology, Formal analysis, Writing – original draft, Visualization. **Sicen Yu:** Investigation, Methodology. **Zhenzhen Yang:** Methodology, Formal analysis. **Hongpeng Gao:** Investigation, Methodology. **Panpan Xu:** Investigation, Methodology. **Guorui Cai:** Methodology, Formal analysis. **Satchit Rose:** Methodology, Formal analysis. **Christopher Brooks:** Investigation, Resources. **Ping Liu:** Investigation, Resources. **Zheng Chen:** Conceptualization, Investigation, Methodology, Formal analysis, Resources, Supervision, Funding acquisition, Writing – review & editing.

#### Declaration of Competing Interest

A patent disclosure (Case # 2022-239) is under filing with UCSD's Office of Innovation and Commercialization.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ensm.2022.06.017.

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