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Selective lithium recovery and integrated preparation of high-purity lithium hydroxide products from spent lithium-ion batteries

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Abstract

The current paper presents an innovative route for selective lithium extraction, followed by production of battery grade LiOH·H\textsubscript{2}O via reductive hydrogen roasting, water leaching and LiOH·H\textsubscript{2}O crystallization. The results suggest that during the initial hydrogen reduction stage, almost 98\% of Li can be transformed into soluble LiOH·H\textsubscript{2}O with H\textsubscript{2} reduction at 500 °C within 15 min, while Ni, Co, Mn all transform into their corresponding insoluble metals or their oxides. Consequently, almost all of Li present in the roasted material can be effectively separated from other impurities by 10 minutes of water leaching at 25 °C with liquid-solid (L/S) ratio of 2, such that the extraction of other metals like Ni, Co, Mn are < 0.1\%. Subsequent stages allow high purity LiOH·H\textsubscript{2}O (99.92\%) to be obtained directly through evaporation and crystallization. In addition, high nickel battery cathode materials (LiNi\textsubscript{0.8}Co\textsubscript{0.1}Mn\textsubscript{0.1}O\textsubscript{2}) are prepared from the recycled LiOH·H\textsubscript{2}O products and these demonstrate good electrochemical performance. Overall, this newly developed hydrogen reduction-based process may provide a more simple, efficient and environmental friendlier method for the recovery of valuable metals from spent LIBs, as well as offering great potential for straightforward industrial-scale recycling.
Keywords: Spent lithium battery; Sustainable recycling; Hydrogen reduction; lithium hydroxides; Clean production

1. Introduction

Spent lithium-ion batteries (LIBs) are a significant waste stream that contain potentially harmful heavy metals, organic chemicals and fluoride-bearing electrolytes [1-4]. According to the overall world market evolution and average life expectancy of LIBs, the predicted global amounts of battery materials ending up to recycling in 2035 will be equivalent to ca. 104 GWh [5-6]. Consequently, this substantial level of waste will pose a serious environmental risk if not dealt with or disposed of properly. Furthermore, considering that spent LIBs contain appreciable levels of valuable metals like cobalt (5 - 20%), nickel (5 - 10%) and lithium (5 - 8%) [7-8], these waste streams are increasingly being investigated globally, not only from an environmental impact perspective, but also as an important secondary source for Ni, Co and Li. It is currently forecast that global Li demand by 2025 will exceed 21 520 t [9], meaning that the scarcity of Li will be an increasingly critical issue within the next decade. As a result, this impeding future supply crisis can only be avoided by achieving high levels of Li recovery (90% minimum) from spent LIBs [10-11], which in turn, requires the development of economically feasible and environmentally sound methods for the separation and recovery of Li from spent LIBs.

Although commercial high-temperature smelting processes that have been utilized by several companies (e.g. Toxco Inc., USA; Sony Corp., Japan; Umicore, Belgium), the focus is primarily on the recovery of high value base metals like Co and Ni, whereas Li recovery is either neglected or only treated as a by-product [12-13]. In addition, hydrometallurgical processes suggested in the scientific literature, typically involve numerous unit processes - such as pretreatment (discharging, dismantling and crushing), acid leaching of waste LIBs with reducing agents (H_2O_2, NaHSO_3, Na_2S_2O_3, D-glucose, ascorbic acid) [14-17], solution
purification [18], solvent extraction of base metals (e.g. Co, Ni, Mn) [19-21] - prior to a final Li recovery step via evaporation and precipitation [15]. It has been subsequently determined that Li losses occur at various points within the complex LIBs recycling flowsheet and that ultimately only ca. 60 to 80% of Li is eventually recovered [22-23]. Alternative leaching methods based on Na$_2$S$_2$O$_8$ oxidation [24], oxalic acid [25-26], tartaric acid [27] and phosphoric acid [28-29] have also been developed in order to preferentially extract Li from spent LIBs, however the high cost of these leaching agents, slow leaching kinetics and the often complicated residue treatment required make upscaling currently unfavorable. Additionally, both classical and newly developed hydrometallurgical processes face challenges related to the treatment of high sodium level wastewaters after the recovery of the target metals (Co, Ni, Mn and Li) from spent LIBs [30].

In order to improve Li recovery, some combined methods such as the reduction roasting with nitrate, sulfate and carbon powders followed by water leaching process have been proposed to preferentially extract Li from LIBs waste [30-32]. The core concept of the roasting approach is to selectively transfer a majority of Li (> 90%) into a water-soluble nitrate [30], sulfate [31], or bicarbonate [32], whilst the other elements remain as non-soluble oxides or metallic elements. Nevertheless, associated emissions like SO$_2$, NO, NO$_2$, CO and CO$_2$ that can be generated during roasting also have significant issues that would need to be solved before the method can be utilized on an industrial-scale. Furthermore, the roasting kinetics of such methods are relatively slow - for example, lithium from cathode materials is only totally converted to lithium nitrate or lithium carbonate with roasting times > 2h [30, 32] - therefore there is an urgent need for the development of alternative LIBs roasting techniques.

This current study proposes a novel LIB recycling method that uses an initial hydrogen reduction step, followed by water leaching in order to selectively extract lithium. Via this
process, almost all of the lithium present can be selectively converted into water-soluble lithium hydroxide within only 15 minutes, whereas the Ni, Co and Mn remain in the form of insoluble stable metals or oxides. Moreover, there is no harmful gas generated in the reduction roasting process, and the separation of lithium can be achieved without any acid and alkali consumption. Another advantage of this process is that battery-grade LiOH·H₂O can be obtained without the requirement for further complicated separation and purification procedures. Currently the demand for lithium hydroxide as a raw material is increasing as high-nickel ternary materials (LiNi₀.₈Co₀.₁Mn₀.₁O₂, LiNi₀.₆Co₀.₂Mn₀.₂O₂) synthesized using lithium hydroxide as a lithium source offer a higher energy density and better charge/discharge performance when compared to those prepared with lithium carbonate [33]. Therefore, this simple and environmentally friendly process for one-step preparation of LiOH·H₂O products from spent LIBs has significant industrial application potential.

2. Experimental

2.1 Materials and characterization

The input materials used in this research were obtained from a battery recycler based in southern China where the spent LIBs had been subjected to a pretreatment - dismantling, sieving, grinding - and it was used in the experiments as received. The mean particle size and specific surface area of the spent LIBs materials, measured by a BT-2002 Laser Particle Size Analyzer, were 12.4 µm and 0.42 m²/g, respectively. The raw material was chemically characterized by ICP-OES (Inductively Coupled Plasma – Optical Emission Spectroscopy, Perkin Elmer Optima DV7100, USA) after the mechanical pre-treatment process to determine the metal elements present and in addition, the total carbon content was measured by a carbon-sulfur analyzer (EMIA-820V, Horiba, Japan). The chemical composition of the spent LIB materials are presented in Table 1, and shows that the main metals present were Ni, Co,
Mn and Li. The characterization of the LIBs waste by XRD (PANalytical X’Pert Pro Powder, Almelo, Netherlands) and SEM (LEO 1450, Carl Zeiss Microscopy GmbH, Jena, Germany) - shown in Fig. 1 - reveals that lithium, cobalt, nickel and manganese exist primarily as LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ with a regular sphere morphology.

Table 1. Chemical composition of the crushed LIB materials used in the study

<table>
<thead>
<tr>
<th>Elements</th>
<th>Li</th>
<th>Co</th>
<th>Cu</th>
<th>Ni</th>
<th>Al</th>
<th>Mn</th>
<th>Fe</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>6.03</td>
<td>10.15</td>
<td>&lt; 0.01</td>
<td>25.64</td>
<td>0.27</td>
<td>13.98</td>
<td>0.03</td>
<td>3.01</td>
</tr>
</tbody>
</table>

Fig.1 (a) XRD patterns and (b) SEM images of the industrially treated spent LIBs materials.

2.2 Experimental procedures

2.2.1 Selective hydrogen reduction roasting

Roasting experiments were performed in a horizontal tube furnace (GRGL1100-18-300, Refan, Shanghai, China) and the temperature was measured by a K-type thermocouple controlled by a Keithley 2000 multimeter intelligent temperature controller (accuracy of ±1°C, Tektronix, Inc., Beaverton, United States). Within the furnace, the flow of hydrogen
gas (99.999 vol.%) was carefully controlled by digital mass flow meters (Alicat Scientific, Inc. Tucson, AZ USA) and different flow rates of H₂ (FLR-H₂; 50 mL/min, 100 mL/min, 150 mL/min, 200 mL/min, 250 mL/min) and roasting durations (2 min, 5 min, 10 min, 20 min, 30 min, 40 min, 60 min) were applied. Samples were placed in an Al₂O₃ crucible prior to insertion into the cold furnace, which was then heated at a rate of 200 °C/h under a protective argon (99.999 vol.%) atmosphere to the predetermined target temperature (between 300 to 600°C). Once the desired temperature was achieved, the gas feed was instantaneously switched from argon to air to initiate the experiment. When the test was complete, the atmosphere was changed back to argon and the furnace was cooled down at a rate of 200 °C/h. The degree of reduction that occurred during the roasting was determined based on the sample mass change measured by weighing before and after the experiments.

2.2.2 Water leaching

Water leaching was performed with a liquid to solid ratio of 20:1 for 30 min at a temperature of 30 °C to evaluate the efficiency of the combined hydrogen reduction roasting process. After determining the optimal roasting conditions for the selective separation of lithium, the influence of the liquid-solid (L/S) ratio (from 1:1 to 20:1) and contact time (from 5 to 60 min) on the water leaching process were studied in more detail. The extraction of Li (%E) was calculated based on the solution samples via Equation 1:

\[
%E = \left( \frac{C_i \times V}{m_o \times w_o} \right) \times 100\% \tag{1}
\]

where \( m_o \) (g) and \( w_o \) (%) are the mass of the input materials and the compositions of element \( i \), respectively; \( C_i \) and \( V \) are the concentration of element \( i \) and the volume of water leaching solution.
The metals content present in the leach residue was analyzed by ICP-OES. In addition, the structure, morphology and composition of the residues before and after leaching were also characterized by XRD and SEM-EDS, respectively.

2.2.3 Preparation of LiOH·H₂O

After the hydrogen reduction roasting and water leaching, 200 mL of the resultant solution obtained was evaporated down to 20 mL at 110 °C, and then cooled to 50 °C in order to prepare lithium hydroxide. The subsequent product was washed by a saturated lithium hydroxide solution with a liquid to solid ratio of 1, before being dried at 80 °C. In order to reduce Al content in the lithium hydroxide produced, the following measures were adopted:

1) Avoidance of complete water evaporation from the obtained leachate;
2) Washing out of aluminum ions contained in the crystalline products with an almost saturated lithium hydroxide solution.

The purity, structure and morphology of lithium hydroxides obtained were analyzed and characterized by ICP-OES, XRD and SEM, respectively. Additionally, the quality of the lithium hydroxides was further investigated by measuring the electrochemical performance of LiNi₀.₈Co₀.₁Mn₀.₁O₂ cathode materials synthesized from the recycled LiOH·H₂O and the results were compared with those obtained from a commercially available lithium hydroxide (99.99 wt.%).

2.2.4 Preparation of cathode materials

Commercial Ni₀.₈Co₀.₁Mn₀.₁(OH)₂ precursors (Fujian Kinslithium Advanced Material Co., Ltd) and commercial LiOH·H₂O (1:1 molar ratio) were added together with absolute ethyl alcohol to form different slurries. These suspensions were then thoroughly mixed for 8 h using a ball mill and the final outputs was vacuum-dried at 100°C for 14 h. Once dry, material was calcinated at 780 °C (heating rate 5 °C min⁻¹) for 20 h under oxygen flow, before being allowed to slowly cool to room temperature to form the cathode materials. N.B. The presence
of excess lithium (ca. 5%) was used to compensate for the lithium loss during the high temperature calcination process. A similar process was also followed with the commercial Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$(OH)$_2$ precursors and recycled LiOH·H$_2$O. The synthesized LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ cathode materials are subsequently labelled as C-NCM811 - based on commercial - and R-NCM811 synthesized from recycled material.

2.2.5 Electrochemical Evaluation

Electrochemical characterization of the samples was performed using two-electrode CR2032-type coin cells at room temperature. Cathode slurries that consisted of 80 wt. % of the two synthesized active cathode materials (C-NCM811 and R-NCM811), 10 wt. % of carbon black, and 10 wt.% of polyvinylidene fluoride were prepared. These mixtures were magnetically stirred for 10 h to obtain separate homogeneous slurries. The slurries were then pasted onto aluminum foil current collectors with a coating machine and the resulting electrodes were dried at 120 °C for 12 h in a vacuum oven prior to use. The electrolyte utilized comprised of 1 M LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) with a 1:1:1 volume ratio. Cells were assembled in an argon filled glove box with a Li anode and Celgard® polypropylene separators. Prepared batteries were measured at room temperature over a voltage range of 2.75 to 4.3 V vs. Li/Li$^+$ using an 8-channel battery analyzer (Neware, China).

3. Results and Discussion

3.1 Hydrogen reduction roasting

The hydrogen reduction roasting of spent LIBs materials were investigated with respect to roasting temperatures and roasting time, H$_2$ flow rate and materials amounts as shown in Fig. 2 (a-d). Roasted materials obtained were treated by water leaching (L/S = 20:1, 30 min, 30 °C)
to evaluate the efficiency of the hydrogen reduction roasting process. The results in Fig. 2a show that an increase in the roasting temperature provides an improved separation of Li from LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$; as temperature is raised from 300 to 500 °C, Li extraction increases significant from 0.65 to 97.68%, and there is almost no Ni, Co and Mn found within the leachate. As can be seen in Fig. 2b, > 97% of Li could be leached from the cathode powders after only 15 min of roasting. When compared to the previously reported nitrate [30], sulfate [31] and carbon reduction [32] roasting processes, the hydrogen reduction roasting process is more efficient both in terms of roasting kinetics and selective extraction of metals. Further studies into the effect of hydrogen flow rate in Fig. 2c, show that the leaching efficiency of Li increased from 37% to 98% as the hydrogen gas flow rate was increased from 50 mL/min to 200 mL/min. In order to obtain the most advantageous separation efficiencies, a hydrogen gas flow rate of 200 mL/min was selected as being optimum in this study. Fig. 2d highlights the effect of the spent LIBs materials surface density (i.e. thickness of the layer in the crucible; kg/m$^2$) on the extraction of Li, Ni, Co and Mn. It was found that the extraction of Li gradually decreased with an increased thickness of the cathode materials as this resulted in a reduction in the available contact area between hydrogen and the spent LIBs sample. Maximum reduction efficiencies of > 97% were evident under the optimum conditions of $T = 500$ °C, $t = 15$ min, $FLR-H_2 = 200$ mL/min, and spent LIBs = 1 kg/m$^2$, whereas the extraction of Ni, Mn and Co remained at approximately < 0.01%.
Fig. 2. Effect of (a) roasting temperature (t = 15 min, FLR-H2 = 200 mL/min, LIBs = 1 kg/m²), (b) roasting time (T = 500 °C, FLR-H2 = 200 mL/min, LIBs = 1 kg/m²), (c) hydrogen flow rate (T = 500 °C, t = 15 min, LIBs = 1 kg/m²) and (d) amount of spent LIBs (T = 500 °C, t = 15 min, FLR-H2 = 200 mL/min) on the extraction of metals (L/S = 20:1, 30 min for water leaching).

The different extraction behaviors of Li and other impurities are mainly attributed to the different product solubilities that result from the reduction roasting. XRD patterns of the roasted LIBs waste - shown in Fig. 3 - clearly reveal that Li in the cathode material (LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2) was transformed into LiOH·H₂O via H₂ reduction at temperatures > 400 °C, whereas the Ni, Mn and Co mainly exist in the metallic form or as their oxides. Results displayed in Fig. 4, also show that no diffraction peaks related to LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 could be identified after hydrogen gas treatment with a flow rate of 150 mL/min, as it was
transformed into LiOH·H₂O, Ni, Co and MnO phases. The diffraction peaks corresponding to lithium hydroxide were observed to disappear after water leaching (Fig. 5), whereas the peaks related to Ni, Co (metals) and Mn (MnO) were still evident in the leach residues although slightly shifted when compared to the as roasted products.

Fig. 3. XRD diffractograms of LIBs samples roasted at different roasting temperatures
**Fig. 4.** XRD diffractograms of roasted samples treated with different hydrogen flow rates.

**Fig. 5.** XRD diffractograms of leaching residues from the water leaching of LIBs samples roasted at different temperatures.
Further analysis of the leaching residue morphologies by SEM (Fig. 6) verified that the increase in temperature led to a change in the particle morphology from a regular spherical shape to an amorphous polyhedron and that the stable LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ structure was almost completely broken down after only 15 min at 500 °C with a 200 mL/min hydrogen gas flow rate. This change in the structure of the cathode materials facilitates the contact between the roasted product and the leaching agent, which further enhances the lithium separation. The results shown in Fig. 2 also indicate that the mass of spent LIBs materials gradually decreased with the increase in temperature even though the associated change in lithium extraction was small. When combined with the XRD results, it can be inferred that the conversion process of waste lithium batteries that occurs during hydrogen reduction process is as follows:

$$\text{LiNi}_{0.5}\text{Mn}_{0.2}\text{Co}_{0.3}\text{O}_2 \rightarrow \text{LiOH}\cdot\text{H}_2\text{O}, \text{MnO}, \text{NiO}, \text{CoO} \rightarrow \text{LiOH}\cdot\text{H}_2\text{O}, \text{MnO}, \text{Ni}, \text{Co} \ (2)$$

The above findings show that a highly selective extraction of Li could be achieved with a H$_2$ flow rate above 200 mL/min and roasting time at 500 °C > 15 min. Almost 98% of the Li in the spent LIBs materials could be separated - a significantly higher level than that achieved in the absence of roasting (60 - 85%) - which clearly demonstrates the benefit of such a roasting step for Li separation.
3.2 Selective leaching of Li from roasted materials

Extraction of Li from the LIBs material roasted under optimum conditions (roasting temperature = 500 °C, FLR-H2 = 200 mL/min, spent LIBs = 1 kg/m² and roasting time = 15 min) by water leaching was investigated at 25 °C with different reaction times (between 2 and 30 min) and L/S ratios of water to roasted sample (1:1 to 12:1 mL/g). As shown by Fig. 7 (a), > 90% of Li dissolves very rapidly during the first 5 min at L/S = 2, after which the dissolution kinetics decrease significantly with only a ca. 3% increase in the level of Li extracted over the subsequent 25 min. In contrast, the extraction of Ni, Co and Mn was found to display only a minor change over the same time period and the overall level of each was < 0.01%. The results in Fig. 7a highlight the solubility of LiOH in water (12.8 g per 100 mL H2O at 20 °C), and that extractions of Li > 97% can be achieved in a relatively short time (t =
10 min) with a modest L/S = 2. Nevertheless, these findings also demonstrate that Li concentration in the leach solution decreased gradually with an increase of L/S (Fig. 7b). For example, when the L/S ratio is 1:1, Li concentration (36.78 g/L) is almost saturated, however, at higher L/S ratios (e.g. 4:1, mL/g), the concentration of Li only reached 16.97 g/L. Taking into account the extraction efficiencies and subsequent preparation of LiOH, the roasted materials were treated at a L/S = 2 for 10 min in order to maximize both the Li concentration (~34 g/L) and extraction efficiency (> 97%).

![Diagram](image1.png)

Fig. 7. Influence of (a) leaching time (L/S = 2:1, mL/g; room temperature) and (b) liquid-solid (L/S) ratio (10 min; room temperature) on Li extraction by water leaching.

The main elements in the leach residues are shown in Fig. 8. The distribution regions of Co, Ni and Mn are coincident and combined with each other without any obvious distribution boundaries, whereas Al clearly exists as separate phases with discernable phase boundaries. In addition, Mn, Al and O are observed to be more closely associated, which is consistent with the XRD analysis results (Fig. 5) that show Mn is mainly present as manganese oxide - although due to the small amount of aluminum, the phases of Al were unable to be detected by XRD analysis. Based on these results, the water leach residue could be treated by an ‘acid
leaching – solvent extraction – evaporation’ process [32] to recover nickel, cobalt and manganese. These materials could then be recycled to prepare further ternary precursors and the $\text{H}_2$ generated during leaching can be captured for use in the roasting stage.

Fig. 8 SEM images and elemental maps of the water leaching residues.

3.3 Lithium hydroxide products

3.3.1 Preparation of lithium hydroxides

The concentration of metals in Li-rich solution obtained from the water leaching process under optimum conditions are presented in Table 2. As can be seen, the lithium could easily reach a high concentration (34.14 g/L) that is close to the saturation point. In addition, the concentrations of Co, Ni, Mn, Cu and Fe were all determined to be lower than 0.01 g/L, whereas about 20% of Al dissolved into the leachate, to give a concentration of approximately 60 mg/L. Following leaching, the pregnant leach solution (PLS) was subjected to evaporative crystallization, washing using saturated lithium hydroxide solution and drying, in order to prepare a lithium hydroxide product. Results from the XRD analysis in Fig. 9a
show that the peaks related to the final product are consistent with LiOH·H$_2$O (standard PDF card JCPDS # 25-0466). Chemical analysis by ICP-OES and acid-base titration following total leaching show that – with the exception of Al (0.008%) – the level of impurity elements are ≤ 0.001% without the use of any additional purification processes. As can be observed in the SEM images, the average particle size of the product is about 10 µm (Fig. 9b) and the LiOH content of the material was determined to be 57.10% - a level that meets the standard required for battery grade LiOH·H$_2$O.

Table 2. Chemical composition of the Li-bearing solution after roasting and leaching.

<table>
<thead>
<tr>
<th>No.</th>
<th>Li</th>
<th>Co</th>
<th>Ni</th>
<th>Mn</th>
<th>Na</th>
<th>Al</th>
<th>Cu</th>
<th>Fe</th>
<th>Ca</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLS1</td>
<td>34.14</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.06</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Fig. 9. Characterization of the prepared LiOH·H$_2$O: (a) Impurities contents of prepared LiOH·H$_2$O with XRD patterns as an inset and (b) SEM images of LiOH·H$_2$O prepared from Li-rich solution.

3.3.2 Electrochemical performance NCM811 prepared using recycled LiOH·H$_2$O

The lithium hydroxide product prepared was subsequently used as a lithium source to prepare high nickel cathode materials (LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$) together with a commercial
precursor \((\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})(\text{OH})_2\). Fig. 10 shows the electrochemical performance of LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 cathode materials that were synthesized using recovered LiOH as the lithium source (denoted as R-NCM811), compared to LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 cathode materials synthesized with commercial LiOH (denoted as C-NCM811).

![Fig. 10](image)

Fig. 10. (a) Initial charge/discharge curves at 0.1 C; (b) dQ/dV at the first cycle; (c) cycling performance at 0.5 C and (d) rate capability at different current densities of C-NCM811 and R-NCM811 electrodes between 2.75 and 4.3 V.

As shown in Fig. 10 (a), the charging and discharging capacity of LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 cathode materials synthesized with commercial LiOH (C-NCM811) is higher than that of LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 cathode materials synthesized with recycled LiOH·H_2O (R-NCM811), although the initial coulomb efficiencies are similar - C-NCM811 90.5% cf. R-NCM811 90.7%. Fig. 10 (b) presents the dQ/dV plots of the C-NCM811 and R-NCM811 for the initial charge and discharge cycle. It is clear that the potential difference of the oxidation/reduction
peaks located at 3.71V for R-NCM811 is larger than that of the C-NCM811, suggesting a substantial polarization of the R-NCM811 electrode occurs. Moreover, Fig. 10 (c) displays the cycling performance of the two electrodes at the rate of 0.5 C in 2.75 - 4.3 V range and the results indicate that the R-NCM811 electrode retains better capacity throughout the whole cycle mainly as a consequence of the stabilizing effect Al to the strong nature of Al-O bonds in contrast to Ni-O or Co-O bonds\cite{34-35}. The rate property of C-NCM811 and R-NCM811 electrodes are displayed in Fig. 10 (d). As the current density is increased, the specific capacity of the two electrodes reduces due to electrochemical polarization. At the 10 C current density, the capacity retention of C-NCM811 electrode is 75% of that at the current density of 0.1C, while in comparison, the capacity retention of the R-NCM811 electrode at 10 C is only 63%. Nevertheless, it was found that the discharge capacity recovery of the two electrodes was close to the initial value when they were returned to 0.1C. This finding indicates that Al contamination within the recycled LiOH has an influence on the rate performance of the LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 cathode material, although the detailed mechanism and extent of this influence requires further investigation.

Based on these results, it can be concluded that the lithium hydroxide products prepared meet the needs of battery-grade lithium hydroxide in terms of purity, particle size and electrochemical performance. Although the presence of Al contamination decreases the performance of rate property of the related NCM811 electrode, the overall cycling property was noticeably enhanced.

4. Conclusions

This research proposes a simple, efficient and environmentally friendly method to selectively extract lithium from spent LIBs and prepare high purity lithium hydroxide products from waste LIBs by ‘hydrogen reduction-water leaching’ followed by an evaporative crystallization process. The findings show that:
(1) Li in the spent LIBs can be easily converted into soluble LiOH·H$_2$O during hydrogen reduction roasting, while Ni, Co, Mn, Al remain as insoluble metal elements or oxides. Compared with other roasting processes (nitrification, carbon reduction and sulfate-based), the hydrogen route is free from harmful gases such as SO$_2$, CO, NO$_x$, etc.

(2) The recovery rate of lithium is high and > 97% of Li can be selectively separated from the other metals present very quickly – reduction roasting for 15 min and water leaching for 10 min. In addition, an ideal lithium hydroxide solution leachate can be achieved without the need for additional enrichment and purification processes.

(3) Battery grade LiOH·H$_2$O (99.92%) could be directly produced from the Li-rich solution by evaporative crystallization. High nickel cathode materials (NCM 811) prepared from the recycled lithium hydroxide products shows good electrochemical performance, especially in during cycling. Additionally, the presence of Al contamination in the recovered LiOH·H$_2$O was observed to result in only a minor reduction in the cathode material performance when compared to a similar commercial-sourced lithium hydroxide.

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1. Selective extraction of Li from waste LIBs by hydrogen roasting, water leaching process.

2. The extraction of other metals like Ni, Co, Mn were < 0.1%.

3. Battery grade LiOH·H₂O could be prepared from the Li-rich water leaching solution.

In this paper, we proposed an innovative route for selective lithium extraction, followed by production of battery grade LiOH·H₂O via reductive hydrogen roasting, water leaching and LiOH·H₂O crystallization. The Li can be achieved selective transformation from spent LIBs to LiOH·H₂O by using hydrogen as reductant at lower temperature. The recovery rate of
lithium is high and > 97% of Li can be selectively separated from the other metals present very quickly – reduction roasting for 15 min and water leaching for 10 min, while the extraction of Ni, Co, Mn are < 0.1%. There is an ideal lithium hydroxide solution leachate can be achieved without the need for complex enrichment and purification processes. Overall, this newly developed hydrogen reduction-based process may provide a more simple, efficient and environmental friendlier method for the recovery of valuable metals from spent LIBs, as well as offering great potential for straightforward industrial-scale recycling.

All of the authors have approved the contents of this paper and have agreed to the submission policies of Separation and Purification Technology. All authors have made substantial contributions to the underlying research and drafting of this manuscript. Additionally, to the best of our knowledge, the named authors have no conflict of interest, financial or otherwise. The authors sincerely believe that the research conducted has the requisite level of scientific and industrial impact that would provide significant interest for the readers of the Separation and Purification Technology. It presents attractive processing option and related phenomena for real industrially crushed battery wastes.

Declaration of Interest Statement

We hereby submit an original research article entitled “Selective lithium recovery and integrated preparation of high-purity lithium hydroxide products from spent lithium-ion batteries” for consideration to be published in Separation and Purification Technology. We confirm that all the figures and tables are the original work and have not been published elsewhere.

All of the authors have approved the contents of this paper and have agreed to the submission policies of Separation and Purification Technology. All authors have made substantial contributions to the underlying research and drafting of this manuscript. The authors declare no competing financial interest or otherwise. The authors sincerely believe that the research conducted has the requisite level of scientific and industrial impact that would provide significant interest for the readers of the Separation and Purification Technology.
Yours, Sincerely,

Fupeng Liu and Co-Authors