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1 Re-purposing of fruit peel waste as a green reductant for 2 recycling of spent lithium ion batteries

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13 KEYWORDS: Spent lithium ion batteries, Orange peel waste, Green reductant, Leaching,

14 Recycling

15 ABSTRACT

16 The development of environmentally-benign hydrometallurgical processes to treat spent lithium
17 ion batteries (LIBs) is a critical aspect of the electronic-waste circular economy. Herein, as an
18 alternative to the highly explosive H_2O_2 , discarded orange peel powder (OP) is valorized as a
19 green reductant for the leaching of industrially produced LIBs scraps in citric acid (H_3Cit) lixiviant.
20 The reductive potential of the cellulosic- and antioxidants-rich OP was validated using the 3,5-
21 dinitrosalicylic acid and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic) acid assays. Leaching
22 parameters such as OP concentration (200mg), processing temperature (100°C), H_3Cit
23 concentration (1.5 M), reaction duration (4 h) and slurry density (25g /ml) were systematically
24 optimized to achieve 80-99% leaching efficiencies of Ni, Mn, Co, and Li from the LIBs "black
25 mass". Importantly, solid side-streams generated by the OP-enabled leaching displayed
26 negligible cytotoxicity in 3 different human cell lines, suggesting that the process is
27 environmentally safe. As a proof-of-concept, $\text{Co}(\text{OH})_2$ was selectively recovered from the green
28 lixiviant and subsequently utilized to fabricate new batches of LiCoO_2 (LCO) coin cell batteries.
29 Galvanostatic charge-discharge test revealed that the regenerated batteries exhibited initial
30 charge and discharge values of 120 mAh/g and 103 mAh/g respectively, which is comparable to

the performance of commercial LCO batteries. The use of fruit peel waste to recover valuable metals from spent LIBs is an effective, ecofriendly and sustainable strategy to minimize the environmental footprint of both waste types.

INTRODUCTION

Lithium ion batteries (LIBs) are currently used in a wide-range of electronic products (e.g. smartphones, notebooks, cameras, electronic vehicles, medical devices, etc.) and have become an indispensable part of our daily life.¹⁻² According to a recent report, the global market value of LIBs is expected to reach a staggering \$139 billion by 2026.³ As the demand for LIBs continue to grow at a rapid pace⁴, so does the pile of spent LIBs waste. However, only 2% and 5% of the LIBs waste are currently recycled per annum in Australia and EU, respectively.⁵⁻⁶ Majority of the spent LIBs often end up in landfills or incinerators, which are both environmentally unfriendly and economically unwise.⁶⁻⁷

LIBs waste contains numerous valuable resources like cobalt (Co), lithium (Li) and other metals that could be recovered and reused. In fact, out of the \$23.51 billion worth of the LIBs that are annually produced, most of the value stems from the metallic constituents.⁸ Current

46 methods to recycle LIBs include pyro-, bio- and hydrometallurgy. Pyrometallurgy, refers to the
47 thermal treatment of the LIBs waste at extremely high temperature ($> 500^{\circ}\text{C}$) to smelt the
48 valuable metals. Although this process is widely used in the industry, it is characteristically
49 energy-intensive and emits a substantial level of hazardous toxic gas.⁹ Comparatively, the use
50 of acid-generating microbes (bacteria/fungi) such as *Acidithiobacillus ferrooxidans*,
51 *Acidithiobacillus thiooxidans*, *Aspergillus niger* to extract heavy metals from the LIBs waste in
52 bio-metallurgy exerts minimal environmental and health impacts.¹⁰⁻¹² However, the industrial
53 adoption of this process is severely curtailed due to the inefficiency of the bio-leaching process,
54 and the susceptibility of the microbes to the toxic effects of the metals.¹³ In contrast,
55 hydrometallurgy, which makes use of water as a solvent, provides a more direct metal recovery
56 route. In terms of the operational conditions, the processing temperatures in hydrometallurgy
57 (10 to 200°C)¹⁴ are significantly lower than pyrometallurgy and its efficiency is independent of
58 the growth kinetics of the microbes. Additionally, the low energy consumption, high recovery rate
59 and ease of operation associated with hydrometallurgy makes it a highly attractive approach to
60 treat LIBs waste.

61 Conventional hydrometallurgical processes rely heavily on the combinatorial use of strong
62 inorganic acids (e.g. H_2SO_4 , HCl , HNO_3) and reductants (e.g. H_2O_2) to leach out metals from
63 spent cathode materials.¹⁵ However, the industrial-scale utilization of strong acids will generate
64 substantial amount of secondary pollutant such as SO_3 , Cl_2 and NO_x , which may pose significant
65 potential safety and health risks. Therefore, several studies have started to explore the use of
66 less hazardous weak organic acids such formic, salicylic, citric, gluconic, itaconic, succinic, and
67 acetic acids to replace the strong acids.¹⁶⁻¹⁸ When combined with H_2O_2 as the reducing agent,
68 these mild organic acids can be as effective as mineral acids and also environmentally-safe. For
69 instance, leaching efficiencies of Li and Co from discarded LiCoO_2 (LCO) in citric acid (H_3Cit)
70 (1.25 M) was reported to increase from 54% to 99% and 25% to 91% respectively when H_2O_2
71 (1.0 vol%) was added to the lixiviant.¹⁹ At an optimized combination of tartaric acid (0.6 mol/ L)
72 and H_2O_2 (3 vol%), selective leaching of Li (99.1%) can be achieved from cathode materials of
73 spent LIBs. Additionally, tartaric acid can also concomitantly function as a precipitation agent for
74 the recovery of cobalt tartrate with purity of 96.4%.²⁰ While the effectiveness of H_2O_2 as a
75 reducing agent is undisputed, its long-term reliance is hardly sustainable since H_2O_2 is highly
76 explosive, hazardous and unstable.²¹ Thus, the search for greener alternatives to H_2O_2 has

77 gained significant traction in recent years. Experiments using alternative inorganic reductants
78 such as sodium thiosulfate²² and sodium bisulfite (NaHSO_3)²³ have shown that conditions can
79 be optimized to achieve 80-90% leaching efficiencies of Li and Co from spent LIBs cathode
80 materials. Nonetheless, the introduction of Na^+ to the lixiviant may contaminate the final
81 recovered products as well as incur additional operational cost for downstream product
82 purification steps.

83 Recently, there is an outburst of interest to valorize organic waste residues produced along
84 the food supply for various applications.²⁴ The total amount of food waste generated in the EU
85 was estimated to be 123 kg/ person/ year, of which, fruit and vegetable wastes (FVW) accounted
86 for about 60%.²⁵ Most of the FVW either gets burnt or be is disposed off in landfills.²⁶ Not only
87 is the current practice of dealing with FVW unsustainable, but also represents a huge wastage
88 of critical resources. Noting that FVW is rich in a plethora of redox-active molecules, such as
89 dietary fibers, catechins, phenolic acids, and flavonoids²⁷, researchers have begun to explore
90 the possible use of this class of “waste material” as a low-cost and sustainable approach to
91 recycle LIBs in the last 5 years. For instance, FVW derivatives such as tea and plant wastes¹⁵,

92 ²⁸, ethanol²⁹, grape seed³⁰ and macadamia shells³¹ were demonstrated to be effective organic
93 reductants to enhance acid leaching of metals from spent LIBs. However, the compositional
94 make-up of untreated FVW is a lot more complex compared to the existing inorganic reductants,
95 which may potentially interfere with the post-leaching recovery of the metals and their
96 downstream applications. Furthermore, to the best of our knowledge, functional applications of
97 the metals extracted with the use of organic reductants has not been demonstrated. The search
98 for greener alternative reducing agents remains a critical research gap in hydrometallurgy that
99 has yet to be fully resolved.

100 To co-tackle the twin challenges of resource depletion and waste accumulation, a novel
101 concept of using fruit peel waste as a possible reducing agent for the recycling of end-of-life LIBs
102 waste is proposed in this work. The purposeful exploitation of fruit-based waste products for the
103 treatment of LIBs waste is termed “waste-for-waste” approach. Specifically, using pulverized
104 orange peel (OP) as a prototypical fruit peel waste, the efficacy and safety of OP as a green
105 reductant for the acid leaching of valuable metals from LIBs cathode materials was examined.
106 Organic H₃Cit lixiviant was chosen because it is biodegradable and has been shown to be

107 effective as a leaching agent under mildly acidic pH.¹⁷ The reductive potential of OP was
108 evaluated and it was shown that under optimized conditions, OP-mediated leaching efficiency
109 of Co, Li, Mn and Ni in LIBs black mass containing lixiviant is comparable to the use of H₂O₂ as
110 the reducing agent. Furthermore, the selective recovery of Co(OH)₂ can be achieved using the
111 OP inspired leaching system, which can subsequently be used to regenerate new batches of
112 LCO coin cells.

113 EXPERIMENTAL SECTION

114 **Materials and Reagents**

115 Citric acid monohydrate, hydrochloric acid fuming 37%, sodium hydroxide pellets, 3,5-
116 dinitrosalicylic acid, anhydrous glucose, and Soxhlet extraction apparatus were purchased from
117 Sigma-Aldrich. Concentrated nitric acid (69%) and WHAT extraction thimble (43×123mm) were
118 purchased from VWR™. Concentrated sulfuric acid (95-97%) and hydrogen peroxide (30% in
119 H₂O) was purchased from Honeywell. ABTS assay kit was purchased from Beyotime, China.
120 Dulbecco's Modified Eagle's Medium (DMEM-High glucose), Fetal Bovine Serum (heat
121 inactivated), and Antibiotic-Antimycotic were purchased from GE Hyclone. Resazurin sodium

122 salt (alarmarBlue) was purchased from Sigma-Aldrich. All chemicals purchased and employed
123 in this study were of analytical grade and solutions were prepared using Milli-Q® ultrapure water.

124 The waste cathode material LCO and spent LIBs were kindly supplied by Nanyang
125 Technological University, School of Mechanical and Aerospace Engineering and School of
126 Material Science and Engineering. SEM images of the LCO and spent LIBs are shown in **Figure**
127 **S1**. The metallic composition of black mass was analyzed using inductively coupled plasma
128 atomic emission spectroscopy (ICP-OES).

129 **Pre-processing of spent LIBs**

130 The spent LCO cylindrical cells have a voltage that ranges from 3.1V to 3.4V. To prevent
131 flame and explosion hazards, the LCO batteries were fully discharged by submerging them in
132 NaCl solution (20 wt%) overnight. The complete discharge of the batteries was confirmed using
133 a battery tester (BT3554). Next, the fully discharged LCO batteries were shredded without prior
134 dismantling using a custom-made shredder designed for battery processing (up to 10 kg/h)
135 under inert gas condition at room temperature. The shredded materials were then kept under
136 exhaust suction overnight prior to being air-dried in a fume cupboard. Finally, the shredded

137 materials were grinded using a commercial food processor (JDC 3 L, 300 W) for approximately
138 1 min and sieved using a 60 μm mesh to remove the plastic constituents. The resultant fine
139 particulate is termed “black mass” and was stored in a desiccator for subsequent
140 experimentations.

141 **Preparation and characterization of OP**

142 The OP was obtained from fresh oranges bought from a local supermarket. The OP was
143 immediately separated from the flesh and cut into pieces (~ 2 to 3 cm in length and ~ 2 to 4 mm
144 in thickness). The samples were then oven-dried for 3 days at a constant temperature of 60 $^{\circ}\text{C}$
145 to ensure complete removal of moisture content. The dried OP was then pulverized and sieved
146 with a #60 mesh (pore size = 250 μm). The composition, elemental analysis, lignocellulosic
147 constituent of OP employed in this study were characterized via established methodologies as
148 shown in **Table S1**.

149 Moisture content of OP was determined by comparing the weight difference before and after
150 the oven drying process. The volatile content was obtained via thermogravimetric analysis (TGA)
151 at a temperature increment rate of 50 $^{\circ}\text{C}$ per min and stabilized at 900 $^{\circ}\text{C}$ under N_2 environment

for 7 min. The ash content was acquired through TGA analysis at a temperature increment rate of 3°C per min until it reached 700°C under O₂ environment. The fixed carbon content was calculated using the following expression:

$$\text{Fixed carbon\%} = 100\% - \text{Moisture\%} - \text{Volatile\%} - \text{Ash\%} \quad (1)$$

The absolute elemental content was determined using the CHNS elemental analyzer. The oxygen content was calculated using the following expression³²:

$$\text{Oxygen\%} = 100\% - \text{C\%} - \text{H\%} - \text{N\%} - \text{S\%} - \text{Ash\%} \quad (2)$$

The lignocellulosic composition of OP was quantified with the established protocols described elsewhere.³³ The cellulose content was calculated using the following expression:

$$\text{Cellulose\%} = 100\% - \text{Extractive\%} - \text{Hemicellulose\%} - \text{Lignin\%} - \text{Ash\%} \quad (3)$$

Reducing sugar measurements

The amount of reducing sugar in the OP samples was determined using the 3,5 dinitrosalicylic acid (DNS) method. To prepare the stock assay solution, DNS (1 g) was added to 2 ml of NaOH (2 M). The assay solution was then mixed with the OP sample solution (2:1 v/v) and boiled for 5 min. Reducing sugar-mediated conversion of the DNS into 3-amino, 5-nitrosalicylic acid can be determined spectroscopically at a maxima absorbance wavelength of

165 540 nm (Molecular Devices SpectraMax M2). The equivalent concentration of reducing sugars
166 (equiv. to g/L glucose) of the OP samples was determined using glucose solutions with pre-
167 determined concentrations as standards.

168 **Antioxidant capacity measurements**

169 The antioxidant capacity (AC) of OP was determined using the ABTS assay kit (Beyotime).
170 Prior to the measurement, a mixture of ABTS and oxidizer stock solution (1:1 v/v) was allowed
171 to age in the dark at room temperature overnight. Next, the assay solution was prepared by
172 diluting the mixture with PBS buffer with a dilution factor of 50. Trolox solutions of various
173 concentrations (up to 0.2 mM) were prepared as per the manufacturer's protocol for
174 normalization purpose. Readings were made on a 96 well format (Nunc™, Thermofisher). Each
175 well contains 10 µl of sample or trolox solution, 200 µl of assay solution reconstituted in 1 M of
176 H₃Cit. After 10 min of vigorous shaking, the absorbance was measured with a high-throughput
177 microplate reader (Molecular Devices SpectraMax M2) at a maxima absorbance wavelength of
178 734 nm. AC was computed and presented as "Antioxidant capacity (equiv. to mM Trolox)".

179 Reductive leaching

180 Leaching performance of OP in either LCO or black mass was examined in H₂Cit lixiviant.
181 All the leaching experiments were conducted in a 100 ml round-bottom flask under reflux (water
182 as cooling agent) and stirring (350 rpm) condition. The volume of the leaching solution (40 ml)
183 applied to all the experimental groups. Upon completion of the leaching experiments, the
184 samples were allowed to cool down for 20 min before they were drawn out and transferred into
185 50 ml centrifuge tubes. Next, the residues were removed completely by ultra-centrifugation at
186 rpm 8500 for 10 min and the lixiviant was additionally passed through a 450 nm polyvinylidene
187 fluoride (PVDF) membrane filter to remove any solid residues. The filtered lixiviant samples were
188 kept at 4°C for further use. To determine the ionic concentration of various metals in the lixiviant
189 (1:500 dilution in deionized (DI) water), inductively coupled plasma atomic emission
190 spectroscopy (ICP OES) was used. Aqua regia was used for normalization purpose.³⁴ The
191 leaching efficiency of each type of metal in the lixiviant can be calculated using the following
192 expression:

$$\text{Leaching efficiency\% (Co, Li, Mn, Ni)} = \frac{\text{Conc. (Co, Li, Mn, Ni) in a sample}}{\text{Conc. (Co, Li, Mn, Ni) in aqua regia}} \times 100 \quad (4)$$

193 **Cell viability assay**

194 The toxic potential of the solid by-products (leaching residues) was examined using the
195 alarmarBlue® cell viability assay in accordance to the manufacture's recommended protocol.
196 Briefly, solid residues after the leaching step was recovered, oven-dried (80°C), and
197 resuspended in water at 3 mg/ml (stock solution) by ultrasonication. To ensure sterility, the
198 solution was under UV light (0.9W) for 2 h prior to use. The panel of cell types used are (i)
199 immortalized human keratinocytes (HaCaT), (ii) primary human dermal fibroblasts (HDF) and
200 (iii) normal human colon mucosal epithelial cell (NCM460). Cells were seeded overnight to reach
201 70% confluency before the samples were treated with the leaching residues at various
202 concentrations (i.e. 20, 50, 80, 100, 200, 500, 1000 µg/ml) for 24 h. Cell viability was determined
203 spectroscopically with fluorescence readout at excitation/emission wavelength of 530/590 nm
204 (Molecular Devices SpectraMax M2) as described earlier.³⁵⁻³⁶

205 ***in situ* precipitation of metal hydroxides**

206 To prepare the leaching solution, 5 g black mass and 1 g OP were mixed with 100 ml 1.5M
207 H₃Cit and allowed to react for 4 h at 100°C. Following which, the leaching solution was
208 centrifuged at 8500 rpm for 10 min. To remove the solid residues, the supernatant was then

209 filtered using a 0.22 μm filter membrane (Nalgene®, Thermo Scientific). NaOH was used to
210 recover Co from the black mass leachate by forming cobalt (II/III) hydroxide ($K_{\text{sp}} = 5.92 \times 10^{-15}$
211 and 1.6×10^{-44} , respectively). To obtain cobalt hydroxide (II/III) with a high purity, the pH of the
212 black mass leachate was firstly adjusted to 12 by addition of NaOH pellets to enable a rapid
213 precipitation of a hydroxide mixture that includes manganese hydroxide ($K_{\text{sp}} = 2 \times 10^{-13}$) and
214 nickel hydroxide ($K_{\text{sp}} = 5.48 \times 10^{-16}$) along with a portion of cobalt hydroxide. Upon completion of
215 the pH adjustment, the solution was immediately placed in the oven at the temperature of 80 °C
216 for 30 min. The resultant supernatant containing cobalt of high purity was then allowed for a
217 subsequent precipitation via addition of ethanol (100%, $v_{\text{ethanol}}/v_{\text{supernatant}} = 1:10$) at the
218 temperature of 80 °C overnight. The solid content was then washed amply by water, collected
219 by centrifugation at 8500 rpm for 10 min, and dried in the oven at 60 °C overnight. Energy-
220 dispersive X-ray spectroscopy (EDX) analysis revealed that the predominant oxides recovered
221 using the OP approach is Co (II) hydroxide (Figure S2).

222 **Regeneration of LCO battery**

223 To synthesize LCO, the recovered cobalt hydroxide was mixed with Li_2CO_3 (atomic ratio of
224 Co/Li = 1:1.1). Excess Li was added to compensate for the thermal decomposition of Li during
225 the thermal treatment.³⁷ The mixture was then calcined at 850°C for 5 h to form LCO. The product
226 after calcination was examined via X-ray diffraction (XRD) to determine its crystal structure.

227 Electrode slurry was prepared by mixing the recovered LCO, super P carbon and PVDF
228 binder (Weight percent ratio: 80:10:10) in N-methyl-2-pyrrolidone (NMP) solvent. The slurry was
229 coated onto an aluminum current collector and dried in the vacuum oven overnight at 90°C. Li
230 ion coin cell batteries were fabricated in an Ar filled glove box (MBRAUN) using this cathode and
231 Li metal as the anode and LiPF_6 in ethylene carbonate (EC) / diethyl carbonate (DEC) as the
232 electrolyte.

233 To assess the cyclic performance of the recycled Li ion coin cell batteries, the batteries were
234 subjected to galvanostatic charge-discharge testing at 0.1 C at a constant rate at room
235 temperature using Neware battery tester. The upper limit of the voltage used in the test was set

to be 5 V and the current was set to range from -1 to 1 mA. Voltage and current data were recorded every 30 seconds.

Statistical analysis

All experiments in this study were carried out with triplicates. Data are presented by mean $\pm$ standard deviation (SD) with p value indicated where necessary. Origin 9 (OriginLab) was used for statistical analysis. Experimental data were subjected to either Student's t-test or one-way analysis of variance (ANOVA) where applicable. Statistical differences are indicated with probability value (p value) in the associated text or figure caption.

RESULTS AND DISCUSSION

Reductive potential of OP waste

It was postulated that the reducing capacity of OP could be attributed to two possible mechanisms of action. The first implicates the "reducing sugar theory", as has been reported in several biomass-mediated leaching processes.³⁸⁻³⁹ When heated under acidic condition, about 30% of the cellulose could be degraded into glucose and over 70% of the hemicellulose could be rapidly converted into aldehyde-containing reducing sugars as xylose, arabinose, and mannose.⁴⁰⁻⁴² Oxidation of glucose can produce polyhydroxyacids, formic, gluconic, aldonic and aldonic acids, aldoses, and CO₂.⁴³⁻⁴⁴ **Figure 1A** depicts the time-dependent production of

253 reducing sugar by the OP samples at 90°C in H₃Cit (1M). As early as 1 h into the reaction, ~ 1.6
254 g/L equivalent concentration of glucose was detected in the reaction mix. The amount of
255 reducing sugar continued to increase with reaction time and plateaus at 3 h with ~ 2.7 g/L
256 equivalent concentration of glucose. Secondly, in addition to its cellulosic-rich composition,
257 another possible source of reducing components could stem from the presence of antioxidants
258 such as phenolic acid and flavonoids, which could be hydrolysed into reducing substances.⁴⁵ As
259 shown in **Figure 1B**, a steady increase in the antioxidant capacity (AC) of OP was observed
260 from 1 h onwards and the maximal AC of 0.108 equiv. to mM Trolox was obtained at around 3
261 h. The slight decrease in the AC of the OP at 4 h may be explained by the thermal instability of
262 antioxidants, which could undergo structural decomposition when heated at 100°C.⁴⁶ Therefore,
263 these findings suggest that OP is a promising H₂O₂ substitute for hydrometallurgical processes
264 as it contains numerous reducing constituents.

265 **Figure 1.** Time-course measurement of **(A)** reducing sugars and **(B)** antioxidant capacity of OP
266 in H₃Cit (1 M). Reaction conditions: OP amount: 200 g; temperature: 90°C.

267 **OP waste as a leaching agent**

268 Having established the reducing properties of OP, the performance of OP as a leaching
269 agent using LCO solution in H₃Cit lixiviant was next evaluated. Experimental group without the
270 addition of OP serves as control. As shown in **Figure 2A**, without the addition of OP, the leaching
271 efficiency of Li and Co from LCO increased with time but only managed to peak at 70% and 75%
272 respectively 24 h into the experiment. In contrast, the leaching efficiencies of Li and Co in the
273 OP-containing lixiviant were clearly enhanced at each time-step relative to the H₃Cit only group.
274 Maximal increment in leaching efficiency of ~ 35% for Li and Co for the OP + H₃Cit group occur

at the 6 h and 8 h mark, respectively. By 24 h, complete (100%) leaching of both metallic ions was observed in the OP + H₃Cit group.

Figure 2. Time-dependent leaching efficiency of **(A)** Co and **(B)** Li in LCO solution using either using either H₃Cit (Δ) or H₃Cit + OP ($\circ$) containing lixiviant. Leaching conditions: 40 ml of H₃Cit (1 M), OP = 200 mg; LCO = 500 mg; reaction temperature: 90 °C. Data are presented as mean $\pm$ standard deviation.

Since the leaching properties of OP have been demonstrated using pure LCO sample, the leaching performance of OP using actual spent LIBs waste (i.e. black mass) was next examined. In terms of chemical composition, black mass is far more complex compared to the LCO sample. ICP OES analysis of the elemental composition of the black mass revealed that apart from Li

(4.7 w%) and Co (35.5 w%), other metallic constituents such as Mn (2.1 w%), Ni (3.1 w%), Al (1.7%), and Cu (1.4%) were also found to be present in the complex waste materials (data not shown). The Al and Cu ions are most likely to originate from the current collectors. **Figure 3** shows the leaching efficiencies of the main cathode materials (i.e. Co, Li, Mn, and Ni) in the LIBs black mass sample. In the H₃Cit only group, the leaching efficiencies of the various metals vary and are limited to <80% regardless of the identity of the metal. Conversely, the addition of OP to the lixiviant resulted in a substantial increase in the amount of extracted metals by ~ 17-30%. Except for Li, which has a leaching efficiency of ~70%, a near 100% recovery of Co, Ni and Mn could be achieved from the OP and H₃Cit containing lixiviant. Taken together, these results show that pulverised OP waste can indeed be exploited to recover cathode metals from not only pristine LCO sample but also actual spent LIB waste.

296 **Figure 3.** Leaching efficiency of (A) Co, (B) Li, (C) Mn and (D) Ni in LIBs black mass-containing
297 lixiviant using either H₃Cit or H₃Cit + OP. Leaching conditions: H₃Cit (1 M), lixiviant volume = 40
298 ml, OP = 200 mg, LCO = 500 mg, black mass = 200 mg, leaching temperature = 90 °C, leaching
299 duration = 7 h. Data are presented as mean $\pm$ standard deviation. * denotes significant difference
300 between the indicated experimental groups. $p < 0.05$.

301 Optimization of OP-mediated leaching conditions

302 The effects of several parameters were systematically examined and correlated to the
303 leaching efficiency of the different metals in the black mass containing lixiviant.

304 *Effect of reductant amount*

305 The effect of varying the amount of OP reductant on the leaching experiments was first
306 examined. H_2O_2 , a widely used reductant in the metal extraction process was employed as a
307 basis of comparison. The amount of the OP and H_2O_2 was varied from 20-400 mg and 50-1600
308 mg per batch of reaction. In general, the leaching efficiency increased with increasing amount
309 of OP and H_2O_2 (**Figure 4**). For the H_2O_2 group, optimal dissolution of the metals was observed
310 with 400 mg (1% v/v) of reductant, which is in agreement with an earlier study that involved the
311 leaching Co, Li, Ni, Cu, Mn, Al from waste LIBs in HCl (4M).⁴⁷ As shown in Figure 4, more than
312 90% of Co, Mn and Ni, and ~ 80% of Li could be recovered at this concentration. However, at
313 higher amount of H_2O_2 , a drastic decrease was observed in the leaching efficiencies for all the
314 metals by as much as 20%. This could be attributed to the concentration-dependent self-
315 decomposition of H_2O_2 which will severely decrease the availability of the reductant (i.e. H_2O_2)

316 in the leaching solution.¹⁴ In the case of the OP group, maximal Co (98.9%), Li (72.5%), Ni
317 (98.2%) and Mn (99.8%), and recovery was observed with 200 mg of OP powder. However, in
318 contrast to the H₂O₂ group, metal leaching efficiencies did not decrease but plateaued at a near-
319 maximal with increasing OP concentration. It should be highlighted that in terms of the leaching
320 efficiency, the potency of both reductants is on par, even if the mass of H₂O₂ are at several-fold
321 higher than the mass of OP used.

322

323 **Figure 4.** Effect of reductant amount on the leaching efficiency of (A) Co, (B) Li, (C) Ni and (D)

324 Mn in LIBs black mass-containing lixiviant using either OP (○) of H₂O₂ (△) as the reductant.

325 Leaching conditions: H₃Cit (1 M), lixiviant volume = 40 ml, black mass = 200 mg, leaching

326 temperature = 90 °C, and leaching duration = 4 h. Data are presented as mean ± standard deviation.

327 *Effect of leaching temperature*

Having established the optimal amount of reductant (i.e. OP= 200 mg and H₂O₂ = 400 mg)

from the previous section, the effect of temperature on the leaching process was next examined.

Temperature has important bearing on the thermodynamics and kinetics of the metal leaching.⁴⁸

Shown in **Figure 5** are the leaching efficiencies of both reductants for Co, Li, Mn and Ni over a

reaction temperature range of 50-100 °C and a reaction time of 4 h. Increasing the leaching

temperature led to a progressive and considerable increase in the leaching efficiency for all the

metallic ions regardless of reductant type. Similar temperature-dependent trend was also

reported by Natarajan et al. with H₂O₂ used as the reductant.⁴⁹ When the leaching temperature

was increased from 50°C to 100°C, a corresponding increase of 55%, 25%, 41% and 47% for

Co, Li, Ni, and Mn was observed respectively. Specifically, at the leaching temperature of 100°C,

82% of Co, 68% of Li, 84% of Ni and 84% of Mn was found to be leached into the lixiviant.

Therefore, with the other parameters kept constant, it can be concluded that 100°C would be the

ideal temperature to maximize the leaching capacity of OP.

341 **Figure 5.** Effect of temperature on the leaching efficiency of (A) Co, (B) Li, (C) Ni and (D) Mn in LIBs
342 black mass-containing lixiviant using either OP (○) of H₂O₂ (Δ) as the reductant. Leaching
343 conditions: H₃Cit (1 M), lixiviant volume = 40 ml, OP = 200 mg, H₂O₂ = 400 mg, black mass = 200 mg,
344 and leaching duration = 4 h. Data are presented as mean ± standard deviation.

345 *Effect of acid concentration*

346 Earlier studies have shown that acid concentration is a critical determinant of the leaching
347 process.^{15, 50} In the proposed leaching systems, an acidic milieu can potentially favour the redox
348 reaction to generate different forms of metallic ions as shown in formula 5. Additionally,
349 increasing the ionic strength of the lixiviant is also postulated to promote the decomposition of
350 cellulose and hemicellulose found in the OP into reducing sugars, thereby aiding the leaching
351 process.⁵¹

352 $Black\ mass(s) + H_3Cit(aq) + OP(s)/H_2O_2(l) \rightarrow$

353 $Co^{2+} + Li^+ + Mn^{2+} + Ni^{2+} + Cit^{3-} + Hcit^{2-} + H_2Cit^- \quad (5)$

354 **Figure 6** shows the plot of leaching efficiency with increasing concentration of H₃Cit from
355 0.1-2.0 M. Highest amount of extracted Co (89%,), Li (76%), Ni (100%) and Mn (100%) occurs
356 when 1.5 M of H₃Cit was used with OP as the reductant. This is consistent with an earlier study
357 by Chen et al. , in which maximal leaching of Co was attained with the same concentration of
358 H₃Cit in 1% H₂O₂.¹⁵ Interestingly, dissolved fraction of Co and Li only improved by ~10% when
359 H₃Cit was increased from 0.2-1.5 M. Comparatively, higher concentration of H₃Cit leads to about
360 25-35% enhancement in Ni and Mn leaching. However, leaching efficiency of these metals

361 began to plateau off or decline slightly in both the OP and H₂O₂-based leaching system when
362 the concentration of H₃Cit was increased from 1.5 M to 2.0 M. A possible explanation could be
363 attributed to formation of insoluble metallic citrates (e.g. Co₃Cit₂) when H₃Cit is added in excess
364 (see formula (6)). Therefore, increasing the H₃Cit concentration to a certain extent is likely to
365 result in the observed level-off/ decline of leaching efficiency by the salting-out effects.⁵²

366
$$M_xH_yCit_z(s) \leftrightarrow M^{a+} + Cit^{3-} + HCit^{2-} + H_2Cit^{-} \quad (6)$$
Where M denotes Mn/ Ni/ Co/ Li; subscript
367 x, y, z denotes the number of the element in the molecule; and superscript a denotes the valency
368 of the different metals.

369 **Figure 6.** Effect of H₃Cit concentration on the leaching efficiency of (A) Co, (B) Li, (C) Ni and (D)
 370 Mn LIBs black mass-containing lixiviant using either OP (○) of H₂O₂ (△) as the reductant.
 371 Leaching conditions: Lixiviant volume = 40 ml, OP = 200 mg, H₂O₂ = 400 mg, black mass = 200
 372 mg, leaching temperature = 100°C and leaching duration = 4 h. Data are presented as mean ±
 373 standard deviation.

374 *Effect of slurry density*

Slurry density was varied by controlling the black mass to the leaching liquid ratio. The slurry density has marginal effect on the leaching efficiency in both the OP and H₂O₂ group till a concentration of 25 g/L (**Figure 7**). Despite the relative high slurry density, the leaching efficiency in the OP group was >90%. However, when the slurry density was further increased from 25 g/L to 32.5 g/L, there was a significant decrease (~15%) in the leaching efficiency for all the metallic ions probed. These findings were corroborated by a number of an earlier works, which similarly showed that slurry densities ranging from 15 to 30 g/L were favourable for leaching of cathode materials.^{15, 49, 53} In addition, the results also suggest that beyond the slurry density of 25 g/L, the amount of H₃Cit and OP may be limiting.

384 **Figure 7.** Effect of slurry density ($w_{\text{black mass}}/v_{\text{leaching solution}}$) on the leaching efficiency of (A) Co, (B)
 385 Li, (C) Ni and (D) Mn LIBs black mass-containing lixiviant using either OP (○) or H₂O₂ (△) as the
 386 reductant. Leaching conditions: H₃Cit (1.5 M), lixiviant volume = 40 ml, OP = 200 mg, H₂O₂ =
 387 400 mg, leaching temperature = 100°C and leaching duration = 4 h. Data are presented as mean ±
 388 standard deviation.

389 Taken together, these findings revealed that the combination of the various parameters: 200
390 mg of OP, leaching temperature of 100 °C, H₃Cit (1.5 M), leaching duration of 4 h and slurry
391 density of 25 g/L could significantly augment the leaching efficiency of the OP-enabled
392 hydrometallurgy. With this set of conditions, Co (91.3%), Li (80.5%), Ni (90.1%) and Mn (92.2%)
393 was recovered from the black mass lixiviant. This set of conditions can serve as a baseline
394 condition for future scale-up and optimization.

395 **Characterization and toxicity evaluation of by-products derived from the leaching process**

396 The sustainable utilization of OP enabled hydrometallurgy would also require that the
397 generated side-streams be environmentally friendly and safe. The elemental composition of the
398 residual materials was first determined using Energy-dispersive X-ray spectroscopy (EDX). As
399 can be seen in **Figure 8A**, the solid by-products contain largely C (64.2%), O (33.3%), and trace
400 amount of Al (1.6%), suggesting that the residue is likely to originate from the anode (graphite)
401 and OP waste (organic compounds). Since the impact of these materials on human health is
402 one key reflection of their environmental footprints, the toxic potential of the solid residues was
403 evaluated using the alamarBlue assay in three different human cell lines, namely, (i) human

404 keratinocytes (HaCaTs), (ii) human colorectal cells (NCM460) and (iii) human dermal fibroblasts
405 (HDF). **Figure 8B** shows the dose response graph of the respective cells that were exposed to
406 the leachate solid waste ranged 0-1000 $\mu\text{g/ml}$. Remarkably, the cytotoxic potential of the by-
407 products was negligible in all the tested cell lines, even at the extreme concentration of 1000
408 $\mu\text{g/ml}$. This suggests that the carbonaceous by-product is non-toxic and by extension, its
409 environmental impact should be minimal. Nevertheless, to better evaluate the long term
410 environmental impact of the OP leaching-derived carbonaceous by-product, other chemical
411 analysis such as Toxicity Characteristic Leaching Procedure (TCLP) can be employed to
412 simulate the leaching process in the landfill setting.⁵⁴

413 **Figure 8. (A)** X-ray fluorescence spectrum of the solid residues by-product. Relative (%)
414 abundance of the detected elements are indicated in the parenthesis. **(B)** Cell viability of HaCaT,
415 HDF and NCM460 exposed to the solid residues at concentrations ranging from 0 to 1000 μg/ml.
416 Data are presented as mean ± SD derived from three independent experiments.

417 **Recovery of Co and regeneration of new lithium ion batteries**

418 To assess the applicability of the OP-enabled hydrometallurgy to the LIBs recycling industry,
419 Co was retrieved from the OP leaching liquor with the aim to be subsequently used to generate
420 new batches of LCO batteries. A two-steps NaOH induced precipitation protocol was employed
421 to retrieve cobaltous hydroxide. In the first step, the pH of the leachate was adjusted to 12 using
422 NaOH to induce rapid precipitation and removal of Mn(OH)_2 and Ni(OH)_2 . At this pH, the
423 precipitation of Cu(OH)_2 and Al(OH)_3 are largely prohibited due to the amphoteric nature of the
424 two hydroxides, which makes them soluble in highly alkaline condition. Thereafter, in the second
425 step, the Co-rich lixiviant was subjected to another round of precipitation using ethanol (100%,
426 $V_{\text{ethanol}}/V_{\text{supernatant}} = 1:10$) to recover cobalt hydroxide. The chemical characteristics of the
427 recovered precipitate was further examined using EDX (**Figure S2**). On the basis of the atomic
428 weight ratio of Co and O, it strongly suggests that the retrieved precipitate is Co(OH)_2 with traces
429 of Al (6.76%) and Cu (1.42%) impurities. Additionally, recovery efficiency of Co across four
430 independent batches of OP leachate displayed good consistency with an average recovery rate
431 of > 73% (**Figure S3**).

432 To prepare LCO, the dried precipitate of $\text{Co}(\text{OH})_2$ was mixed with lithium carbonate (atomic
433 ratio = 1:1.1) and subjected to thermal treatment at 850 °C for 5 h. Successful formation of single-
434 phase LCO (rhombohedral R3m space group crystal system) was validated by examining the
435 crystal structure of the calcined product via X-ray Powder Diffraction (XRD). The XRD diffraction
436 pattern of the calcined materials exhibited a good match with the commercial LCO (**Figure 9A**).
437 Coin cell batteries were assembled using the recycled LCO as the cathode material. Battery
438 performance was evaluated using the galvanostatic charge-discharge test. Cyclic performance
439 data revealed that the newly generated LIBs from the black mass samples possessed a
440 comparable initial charge capacity to the commercial LIBs (~ 120 mAh/g) and the initial discharge
441 capacity was approx. 103 mAh/g (**Figure 9B**). Further analysis revealed the recycled LIBs had a
442 desirable stable performance within 10 cycles of charge and discharge, with less than 20%
443 capacity lost in the 10th cycle (**Figure 9C**). This suggests that this new technology is practically
444 feasible for recycling spent LIBs in the industrial sense.

445 **Figure 9.** (A) XRD pattern of the commercial (blue) and regenerated (red) LCO. (B) The initial
446 (A) charge (blue) -discharge (red) performance of the regenerated LCO coin cell and (C) stability
447 of discharge capacity over 10 cycles of charge and discharge.

448 In summary, the novel use of pulverized OP as an organic, low-cost, and effective green
449 reductant for the recovery of cathodic metals from spent LIBs was demonstrated (Figure 10).
450 The reductive potential of OP can be attributed to the thermal conversion of cellulose to reducing
451 sugars as well as the presence of naturally occurring antioxidants such as flavonoids and
452 phenolic acids. Addition of OP notably enhanced the leaching performance of H₃Cit lixiviant to
453 obtain a 100% extraction yield of Co and Li from pure LCO samples. Both H₂O₂ and OP
454 reductants showed comparable recovery efficacy of Co, Li, Ni and Mn or around 90% in LIBs
455 black mass-containing leaching liquor, even at a relatively high slurry density of 25 g/ml. Further

456 studies are warranted to improve the leaching efficiency the OP approach. Among the possible
457 strategies may include the optimization of stirring speed and leaching time to increase the
458 homogeneity of the leaching suspension, as well as the adoption of a continuous flow set-up to
459 precisely control the flow rate of the feed reactants. Importantly, solid residual generated from
460 the OP-enabled hydrometallurgy process was found to be non-toxic, suggesting that the
461 approach is environmentally sound. Although not covered in this work, clarifying the reusability
462 of the generated OP solid waste for follow-up leaching process would be of interest, since this
463 can potentially further lower the operational cost. Finally, to “close-the-waste-loop”, a two-steps
464 precipitation process was employed to selectively retrieve $\text{Co}(\text{OH})_2$ from the leachate to prepare
465 single-phased LCO, from which, new batches of functional LCO coin cell batteries were
466 regenerated. However, the performance characteristics of the recycled battery can be further
467 improved as the presence of Cu and Al may have affected the overall rated performance of the
468 battery. Targeted removal of Cu and Al may be facilitated by pH adjustment to control the
469 solubility of the metal hydroxides⁵⁵⁻⁵⁶ or use of carboxylate or bipyridine ligands.⁵⁷ Furthermore,
470 this “waste-for-waste” approach could also potentially be extended to other types of cellulosic-
471 rich FVW, as well as lithium ion battery types (e.g. lithium manganese oxide (LMO), lithium nickel

manganese cobalt oxide (LMCO), etc) for the new circular economy of E-waste, so that our lives can be powered in a greener and more sustainable manner.

Figure 10. Mechanistic and process summary of OP-enabled recycling of spent LIBs.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS

Publications website at DOI: XXX. brief description (PDF)

Table S1. Compositional analysis of orange peel (OP)

Figure S1. SEM images of (A) pure LCO and (B) LIBs black mass

Figure S2. X-ray fluorescence spectrum of the recovered cobalt hydroxide

481 **Figure S3.** Recovery efficiency of Co retrieved from 4 different batches of the OP leaching
482 solution

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503 ABBREVIATIONS

504 AC, antioxidant capacity; ANOVA, one-way analysis of variance; H₃Cit, citric acid; DEC, diethyl
505 carbonate; DNS, 3,5 dinitrosalicylic acid solution; EC, in ethylene carbonate; EDX, Energy-dispersive X-
506 ray spectroscopy; FVW, fruits and vegetables waste; HaCaT, immortalized human keratinocytes; HDF,
507 primary human dermal fibroblasts; ICP OES, inductively coupled plasma atomic emission spectroscopy;
508 LIBs, lithium ion batteries; NCM460, normal human colon mucosal epithelial cell; NMP, N-Methyl-2-
509 pyrrolidone; OP, orange peel; SD, standard deviation; TGA, thermogravimetric analysis; W-for-W, waste
510 for waste; XRD, X-ray diffraction,

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649 GRAPHICAL ABSTRACT