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**Challenging the concept of electrochemical discharge using salt solutions for lithium-ion
batteries recycling**

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Abstract

The use of lithium-ion batteries (LIB) has grown significantly in recent years, making them a promising source of secondary raw materials due to their rich composition of valuable materials such as Co, Ni and Al. However, the high voltage and reactive components of LIBs pose safety hazards during crushing stages in recycling processes, and during storage and transportation. Electrochemical discharge by immersion of spent batteries in salt solutions has been generally accepted as a robust and straightforward discharging step to address these potential hazards. Nonetheless, there is no clear evidence in the literature to support the use of electrochemical discharge in real systems, neither are there clear indications of the real-world limitations of this practice. To that aim, this work presents a series of experiments systematically conducted to study the behavior of LIBs during electrochemical discharge in salt solutions. In the first part of this study, a LIB sample was discharged *ex-situ* using Pt wires connected to the battery poles and submerged into the electrolyte solution on the opposite end. The evolution of voltage in the battery was measured for solutions of NaCl, NaSO₄, FeSO₄, and ZnSO₄. The results indicate that, among the electrolytes used in the present study, NaCl solution is the most effective for LIBs discharge. The discharge of LIB using sulfate salts is however only possible with the aid of stirring, as deposition of solid precipitated on the electrodes hinder the electrochemical discharge. Furthermore,

26 it was found that the addition of particulates of Fe or Zn as sacrificial metal further enhances the
27 discharging rate, likely due to an increased contact area with the electrolyte solution. While these
28 findings support the idea of using electrochemical discharge as a pre-treatment of LIBs, severe
29 corrosion of the battery poles was observed upon direct immersion of batteries into electrolyte
30 solutions,. Prevention of such corrosion requires further research efforts, perhaps focused on a new
31 design-for-recycling approach of LIBs.

32

33 *Keywords: Lithium-ion battery; discharging; safety; recycling; corrosion*

34

35 **1 Introduction**

36 Lithium-ion batteries (LIBs) have recently gained popularity due to a massive increase in demand
37 of portable electronic devices such as laptops and mobile phones. In addition, the number of electric
38 vehicles on the roads is forecasted to rise significantly in the near future (Majeau-Bettez et al.,
39 2011; Scorsati et al., 2010), due to stricter environmental legislation aiming to reduce the use of
40 fossil fuels and an increased awareness of the general public (Fultton, 2011). LIBs are currently the
41 preferred source of energy for mobile devices and electric cars as they offer high voltage, high
42 energy density, low self-discharge potential and absence of memory effect (Nie et al., 2015; Li et
43 al., 2016; *Lu* et al., 2013). Considering the aforementioned points, it is expected that the share of
44 LIBs in the field of rechargeable batteries will grow in the future, with the eventual increase in the
45 number of end-of-life LIBs.

46

47 Batteries in general, and LIBs in particular, have complex material compositions in which valuable
48 metals can be found, such as Cu, Li, Co and Ni (Espinosa et al., 2004; Xu et al., 2008; Georgi-
49 Maschler et al., 2012). There is thus a strong interest on the recovery of such metals (Chen et al.,
50 2017). Rare earth elements (REE) are other interesting materials that can also be found in battery

51 scrap, as they are considered critical resources due to their high supply risk and economic
52 importance (European Commission, 2014). Furthermore, the collection and recycling of batteries is
53 important not only due to the valuable materials they contain, but also because of their possible
54 negative environmental impact. Under certain conditions, battery scrap can be considered as toxic
55 or hazardous metallic waste (Chen et al., 2011; Zhang et al., 2013) or may contain corrosive and
56 flammable electrolytes (Nan et al., 2006). In addition, under the current recycling practices, battery
57 scrap is often a mixture of different types of batteries such as nickel-metal hydride (NiMH) or
58 nickel-cadmium cells (NiCd) which contain toxic metals, like Cd and Hg (Lund, 2001). For the
59 reasons mentioned above, there are important economic and environmental drivers to develop
60 efficient systems for battery recycling.

61

62 Typically, the structure of all batteries is similar, regardless of the battery type or chemistry, and
63 consists of the following main components: anode and cathode, a separator to keep these electrodes
64 apart, an electrolyte, and an outer shell for protection. Currently, most recycling processes involve
65 the crushing of batteries to liberate the valuable contents from their outer shell, which is commonly
66 made of plastic or steel (Georgi-Maschler, 2012). However, when a battery is crushed, there is a
67 risk that the anode and cathode will contact each other, creating a short circuit that releases any
68 stored chemical energy. Such a sudden release of energy may be forceful and violent, causing an
69 abrupt rise of temperature (Linden, 2002), strong gas evolution and fires (Li et al., 2010) or
70 explosions (Lee et al., 2002). This risk is most acute with LIBs, because of their high voltage and
71 the high reactivity of its components (Archuleta, 1995; Sonoc et al., 2015).

72

73 To minimize the risks during crushing of LIBs, various approaches have been suggested. Some
74 solutions include freezing LIBs with liquid nitrogen before crushing (Li et al., 2010) or processing
75 the batteries in an inert atmosphere, either under vacuum or in the presence of inert gases like Ar or

76 CO₂ (Lain, 2001; Tedjar et al., 2007). Another option is to crush a limited flow stream of batteries,
77 with the aim of minimizing the impact in the processing plant when some of them explode. All of
78 these approaches are, however, cumbersome, expensive and consume valuable resources (Sonoc et
79 al., 2015). In addition, these practices do not account for the hazardous potential during storage and
80 transportation. Indeed, it is a common practice nowadays to collect and store spent batteries of a
81 mixed composition in a non-organized manner, which results in the risk of short-circuiting due to
82 unwanted contact between batteries or due to possible defects in damaged battery cases. Stored
83 LIBs have been attributed to be the cause of fires in recycling plants, warehouses, and during
84 transportation (Wang et al., 2012). Such fires have been attributed, for example, to accidental short
85 circuiting due to the absence of suitable containers in the presence of water (Lisbona et al., 2011).

86
87 One possible solution for this problem is to completely discharge the batteries before handling, as
88 this would release all chemical energy stored, rendering the battery unreactive (Ra et al., 2006;
89 Krüger et al., 2014). Discharging could also affect the safety of the crushing steps in a positive
90 manner, perhaps even reducing costs associated with additional security measures. One option is to
91 discharge batteries using an external resistor, but this would require strenuous manual labor at
92 industrial scale. To ensure the economic viability of the discharging step, the method used should
93 be capable of discharging batteries from various manufacturers in bulk. One suggested method to
94 discharge batteries in large volumes is submerging them into a salt solution, as it is expected that
95 the combined effect of short circuiting and electrolysis of salt solution will drain the charge of a
96 battery (Lu et al., 2013).

97
98 In previously published literature, several authors have claimed that the electrochemical discharging
99 of batteries in recycling plants is a process well known and commonly used (Li et al., 2016), that it
100 can be performed without major challenges (Ra et al., 2006), is relatively fast (Lu et al., 2013) and

101 requires easily available resources (Zhang et al., 2013; Zang et al., 2013). Nevertheless, descriptions
102 published in the literature are vague and offer neither evidence on the alleged procedures used, nor
103 details of the specific experimental setups utilized (Lu et al., 2013). Such lack of experimental
104 details raises various questions on the feasibility of electrochemical discharge as a pre-processing
105 step for LIBs recycling in real processes. As discharging appears to be a fundamental step on the
106 pre-processing of LIBs, the work hereby presented focuses on the systematic study of the potential
107 conditions for their electrochemical discharge. To the best of the authors' knowledge, this is the
108 first critical study of electrochemical discharge of LIBs using salt solutions. The analysis of the
109 discharging behavior of LIBs using different electrolyte solutions, either stagnant or under stirring,
110 and in the presence or absence of sacrificial metal is presented. Based on the experimental results, it
111 is intended to define the potential and limitations on the use of salt electrolytes for LIB discharge,
112 and thus determine whether this is a suitable alternative, as has been previously suggested and, so
113 far, generally accepted. Although it would be useful to expand this study on batteries other than
114 LIBs (with a voltage of ca. 4V), the electric potential in other batteries such as NiMH or alkaline
115 batteries (1.2V and 1.5V, respectively; Linden et al., 2002), is not high enough to produce an
116 efficient discharge reaction. Thus, other battery types are not included in the scope of this work.

117

118

119 **2 Experimental methods**

120 The first set of experiments was performed using external Pt wires connected to the poles of the
121 battery and submerged in aqueous salt solution contained in a stirred beaker, thus closing the circuit
122 (Fig. 1A). Pt wires were selected for this study as this metal has a naturally high corrosion
123 resistance and does not take part on the electrochemical reactions. The salt solution in this case
124 acted as a controlled short circuit or as a primitive resistor, discharging the battery. Using this setup,
125 the battery was not placed in direct contact with the electrolyte solution and thus, its physical

126 integrity was not compromised. Using this approach, it was possible to monitor the evolution of the
127 electrical potential of the LIB due only to electrochemical discharge (i.e., not attributable to
128 physical damage to the battery). This setup allows the study on the discharging potential of the
129 electrolyte solution and its associated kinetics. The battery discharge was monitored by a
130 continuous measurement of voltage using an IviumStat potentiostat (Teamator, Sweeden).

131

132 To ensure comparability of the experiments, all measurements of discharge *ex-situ* were conducted
133 using the same individual rechargeable LIB obtained from a BL-4B 3.7 V mobile phone (Nokia,
134 Finland) with nominal capacity of 700 mAh that was fully charged between experiments. It is worth
135 pointing out that LIBs are non-uniform products and the discharge behavior will likely vary
136 depending on the chemistry of the battery and its manufacturer. While the measurements hereby
137 presented belong to the specific battery used, they offer experimental results that can be used for
138 comparison of discharging conditions, providing a starting point for the discussion on LIB
139 discharge.

140

141 In a subsequent series of experiments, batteries were directly submerged in the salt solution. In such
142 experiments, two more LIBs were used, namely BL-4C 3.7 V 860 mAh and BL-5C 3.7 V 1020
143 mAh (Nokia, Finland). For elemental analysis, it was decided to study LIBs from different
144 manufacturers: an EB425161LU 3.7 V 1500 mAh (Samsung, South Korea) and BL-4CT 3.7 V 860
145 mAh (Nokia, Finland). All experiments were carried out at room temperature and no artificial gas
146 atmosphere was applied.

147

148 The salt solutions initially chosen for the experiments were NaCl (Merck, p.a.), NaSO₄ (FF-
149 Chemicals, p.a.), FeSO₄ (Rieder-de Haën p.a.) and ZnSO₄ (J.T. Baker p.a.). The salts were
150 dissolved in ultra-pure, de-ionized water. For each of these salts, solutions with three different

151 concentrations (5 wt%, 10 wt% and 20 wt%) were produced, the only exception being NaSO₄ since
152 20% is over its saturation limit and therefore, only 5 and 10% solutions are reported. The
153 aforementioned concentrations were selected for comparison with previously reported data (Lu et
154 al., 2013; Li et al., 2016). These experiments were performed without stirring. In the case of NaSO₄
155 where no full discharge was obtained with a stagnant solution, stirring was introduced into system
156 with a speed of 600 RPM.

157

158 In the second experimental series, the discharge was accelerated by using cathodic protection. In
159 practice, this means the introduction of an additional metallic element into the system, which should
160 corrode preferably over the battery connectors. In an industrial setting, these elements could also
161 provide the potential to redirect the energy retrieved from a battery to a different use, providing the
162 possibility to harvest energy as a by-product. Similar studies have been performed by Nie et al.
163 (2015) and Nan et al. (2006). Metals chosen for cathodic protection were Fe chips (LECO,
164 Germany) with particle size of < 2 mm and Zn powder (Boliden, Finland). The metallic species
165 chosen for cathodic protection were selected based on their occurrence in many different battery
166 types. The two different particle sizes of the metallic particles were selected to study whether this
167 parameter also has an influence on discharge. In these experiments, the Pt wires were placed in
168 direct contact with the metallic component submerged in salt solution, as shown in [Fig. 1B](#).

169

170 The last set of experiments was carried out by submerging the battery samples into the electrolyte
171 solution to simulate the industrial application method suggested by other authors (e.g., Lu et al.
172 2013) and to observe the effect of corrosion on the battery. Fully charged LIBs were submerged,
173 first into a 20% NaCl solution, and later into solutions with added Fe flakes and Zn powder. These
174 experiments were only performed in 20% NaCl solution since this was the electrolyte offering the
175 fastest discharge, as will be detailed in Section 3. In the case of direct battery submersion,

176 corrosion in the poles was observed. To get a better understanding of components that can be
177 corroded during discharge, analysis with X-ray fluorescence (XRF) X-MET5000 (by Oxford
178 Instruments) was performed with the aim of gaining insight towards potential improvements in the
179 discharging process or the battery design.

180 **3 Results and discussion**

181 The first set of experiments was performed to observe the basic discharging phenomena claimed to
182 happen using NaCl salt solutions widely reported in the literature (Lu et al., 2013; Chagnes and
183 Swiatowska 2015; Zhang et al., 2013; Zang et al., 2013). It is reasonable to assume that the battery
184 is discharged by H₂ gas formation at the cathode, which in pure water solutions would be the result
185 of the following water splitting half reactions (Zumdahl and Zumdahl 2000):

186

188

190

191 Although the water splitting reactions require a theoretical potential of 1.23 V, a higher voltage may
192 be needed in reality. The actual value depends on the electrocatalyst material and, in the case of Pt
193 catalyst, it has been reported as 1.68 V (Millet et al., 2010). During electrochemical discharge in
194 aqueous solutions, reactions (1) and (2) are responsible of the consumption of electrons from the
195 cell. Consequently, the battery potential needs to be higher than 1.68 V to drive the water splitting
196 reaction. In the case of LIBs, this condition is easily met, as a fully charged battery has typically an
197 initial potential of ca. 4 V. On the other hand, the lower voltage in other battery types such as Ni-
198 MH and alkaline (1.35 and 1.5, respectively) is not sufficient to promote their discharge in aqueous
199 solutions. It is worth noting that pure water is a poor conductor and it is usually necessary to
200 increase its conductivity, for example with the addition of salts. In previous works, NaCl solutions

has been claimed to be a suitable electrolyte (Lu et al., 2013; Chagnes and Swiatowska 2015; Zhang et al., 2013; Zang et al., 2013) and therefore it is also used in this study as benchmark. However, it is worth pointing out that in a NaCl solution, the risk of a compensating reaction leading to chlorine formation is present:

205

207

Even though the electrochemical potential in Reaction 3 is higher than that of the water splitting reactions, the latter have a higher over-potential (Zumdahl and Zumdahl 2000), in this context defined as the rate limiting steps related to diffusion of species and its associated transfer of electrons (Shen et al., 2011). Consequently, the formation of chlorine gas cannot be overruled in a solution that contains both water and chlorine salt. To eliminate the risks resulting from chlorine gas formation, three sulphate-based salts were explored as electrolytes in this work: NaSO₄, as it has the same anion than NaCl, as well as FeSO₄ and ZnSO₄ since its cations contain metallic elements typically found in battery casings and are thus already present in the recycling process. As will be detailed in Section 3.3, particles of these same metals (Fe and Zn) were applied as “cathodic protection” in experiments with added metal powders to limit the possible reactions occurring in the discharging step.

219

220 **3.1 Effect of salt type and concentration**

The discharging profiles as a function of time for a LIB in 4 different electrolyte solutions at various salt concentrations are presented in Fig. 2. As seen, the time to fully discharge a battery at different NaCl concentrations were 9.0 h, 5.0 h, and 4.4 h for the 5, 10 and 20 wt% solutions, respectively (Fig. 2A). Throughout the discharging experiment, only gaseous products were observed on both Pt wires, and no visible precipitate were formed (Fig. 3A). As seen in Fig. 2A,

226 after an induction time period, there is a sudden drop in the cell voltage resulting in a complete
227 discharge of the batteries, with a final voltage below 1.6 V. In the previously published literature,
228 the reported values of discharging time are widely scattered among different research groups. Zhang
229 et al., (2013) reported that a full discharge was achieved in 24 h using a 5% NaCl solution. On the
230 other hand, Lu et al., (2013) claimed that less than 10 min were required to discharge LIBs when
231 submerged in a 10% NaCl solution, while 70 min were necessary for dilute (i.e., 1%) solutions. The
232 latter authors also present a voltage evolution graph of the discharge at 10 wt% solution that
233 resembles the shape of the curve obtained in the present study (Fig. 2A). One of the reasons for the
234 reportedly faster discharge in the work of Lu et al., (2013) may be that direct submersion of the
235 battery results in a more strenuous discharge than using external Pt connectors. Unfortunately, the
236 aforementioned studies do not offer sufficient details regarding their experiments, including battery
237 manufacturer and type, or measuring procedure for voltage evolution and thus, it is not possible to
238 further evaluate the reasons for such scattered results. Indeed, the different compositions and
239 standards used by LIB manufactures, may result in different discharge rates and is a further
240 complication to the implementation of electrochemical discharge at industrial scale.

241

242 As seen from the profile obtained with NaSO₄ solution (Fig. 2B), the change in the salt anion from
243 chloride to sulfate significantly affected the discharge behavior of LIBs. Not only were longer
244 induction times required, but it was also found that the batteries were only partially discharged with
245 NaSO₄ salt solution, reaching a plateau at around 3 V. Interestingly, the fast formation of a reddish-
246 color precipitate in the solution was observed during these experiments (Fig 3B). It is reasonable to
247 assume that such precipitate blocks the reaction sites at the Pt wires, thus preventing a full battery
248 discharge. The color of the precipitate suggests that it is some type of solid sodium sulfate (Na₂S_x;
249 Steudel 2003), however, detailed analysis was not in the scope of this work. As seen in Fig. 2B, the
250 discharge in NaSO₄ solution initiates after a longer induction time with the higher concentrated

251 electrolyte (10%) compared with the 5% solution, perhaps due to a faster formation of the
252 precipitate, thus inhibiting the battery discharge. This is a reasonable explanation, as it is well
253 established that the rate of formation of precipitates depends on the salt concentration.

254

255 With respect to the use of FeSO₄, the results in Fig. 2C indicate that the discharging reaction is
256 slower compared to NaCl (Fig. 2A), although the curves show certain similarities. The
257 concentration of FeSO₄ in solution appears to play a significant role in the reaction time, although
258 once the discharging begins, the voltage evolution resemble each other. In this case, a precipitate
259 was formed on the surface of the Pt connectors (Fig. 3C) that may have contributed in limiting the
260 rate and extent of discharge (Fig. 2C). Under all concentrations of FeSO₄ hereby studied, the voltage
261 stabilized at around 1 V, a phenomenon that can be attributed to the solid precipitate blocking the
262 gas production. The possible reaction occurring at the anode could be the reduction of Fe²⁺ ions
263 from the solution:

264

266

267 In the case of ZnSO₄ (Fig. 2D), after an initial battery discharge the voltage stabilized at around 3V.
268 During the experiments with ZnSO₄, a rapid formation of a gray solid compound on the anode wire
269 was observed (Fig. 3D), likely blocking the Pt active sites in a similar fashion to FeSO₄. The
270 possible reaction occurring is the reduction of dissolved anions into metallic Zn at the anode:

271

273

274 The formation of metallic Zn is substantiated by the grey hue of the precipitate (Zumdahl and
275 Zumdahl 2000), while the reaction at the other electrode remains as hydrogen evolution (Reaction

276 2). An interesting observation in the case of ZnSO_4 is that no discharge was measured when a 10%
277 solution was used, while a decrease in voltage was observed at both higher (20%) and lower (5%)
278 concentrations. The reason may be associated with the rate of precipitation at the electrodes. Indeed,
279 in the particular case of 10% ZnSO_4 (Fig. 2D), the formation of the solid precipitate was fast,
280 inhibiting the electrochemical reactions even from early stages of the process. Although precipitate
281 formation was also observed at the lower concentration (5 wt%), the growth of Zn precipitate was
282 slower, allowing the discharge of LIBs down to ca. 3 V. On the other hand, with the highly
283 concentrated solution (20%), the voltage drop may have been fast enough to start before the
284 formation of the precipitate, although the plateau was also reached faster due to the eventual
285 formation of precipitate on the Pt wire.

286

287 In summary, NaCl provides an efficient media for discharging batteries since it does not result in
288 precipitate formation. None of the sulfate salt solutions was able to entirely discharge the batteries,
289 likely due to precipitate deposition on the Pt connectors. As seen in Fig. 2, in most cases a small
290 decrease in cell voltage was obtained, followed by a sharp drop in the cell voltage or a plateau
291 depending on the salt solution. For all salts solutions, increasing the salt concentration reduced the
292 required discharging time., with the exception of ZnSO_4 at 10%. Nevertheless, since it is not
293 entirely possible to rule out the formation of chlorine gas from the NaCl solutions, a different
294 approach is evaluated in the following Section to use sulfate salt solutions with the aim of
295 eliminating the accumulation of precipitate on the electrode reactive sites.

296

297 3.2 Discharge in stirred solutions

298 As mentioned in Section 3.1, it was inferred that the inability of sulfate salt solutions to fully
299 discharge the LIBs was related to the deposition of precipitates on the electrode wires. To study if
300 the discharge can be enhanced by preventing the accumulation of this precipitates (Fig. 2),

301 discharge experiments using NaSO₄ solutions at 5 and 10% were carried out with the aid of a
302 magnetic stirrer rotating at 600 rpm. Interestingly, the discharging rate was significantly improved,
303 as observed in the results presented in Fig. 4.

304

305 For comparison, Fig. 4 also presents the results of experiments using NaSO₄ electrolyte without
306 stirring. As mentioned in Section 3.1, the discharge reached a plateau around 3 V, attributed to
307 precipitate formation on the Pt wires. However, when stirring is applied, the precipitate was
308 dispersed in the electrolyte solution instead of blocking the wires, thus allowing a full battery
309 discharge. At a concentration of 5%, the decrease in voltage initiates at the same time with and
310 without stirring, but with stirring a full battery discharge is obtained after 9.3 h. For 10% NaSO₄
311 solution, the discharge was completed after 3.1 h with stirring, an even shorter time than in the non-
312 stirred NaCl solution (Fig. 2A). These results clearly support the hypothesis that precipitate
313 deposition on the Pt electrodes is the responsible phenomenon of an inefficient battery discharge.
314 As was discussed in case of NaSO₄ without stirring (Fig. 2B), the rate of precipitate formation is
315 enhanced at higher electrolyte concentrations. However, since stirring prevents deposition of solids
316 on the electrodes, the influence of salt concentrations is analogous to the case with NaCl: with
317 higher concentrations, a faster movement of ions and gas evolution is expected, resulting in a
318 quicker discharge. These results confirm that, in cases where chlorine gas formation cannot be
319 tolerated, it is possible to fully discharge the batteries using NaSO₄ solution as an electrolyte,
320 provided deposition of precipitates is prevented, e.g., with stirring.

321 3.3 Discharge in the presence of metal particles

322 The second phase of the experimental work hereby presented was to introduce an additional
323 metallic component into the system to provide an additional possibility upon which the energy of a
324 battery can be redirected, potentially accelerating the discharging process. The use of metallic
325 additives in battery discharging processes have been published previously: Nan et al., (2006)

326 reportedly discharged NiMH batteries in 30 min using water as electrolyte and a substance
327 described as “electric iron powder”, while Nie et al., (2015) used a NaSO₄ solution in the presence
328 of Fe powder to discharge LIBs in 24 h. In the present work, the effect of two different metallic
329 species was studied and they were selected to be the same metals used in the salt solutions (Fe and
330 Zn in the form of flakes and powder, respectively). For the electrolyte, a 20% NaCl solution was
331 selected since it provided the fastest discharge, as discussed in Section 3.1. Fig. 5 and 6 show the
332 discharge curves obtained in the presence of Fe and Zn powders, respectively. In addition,
333 photographs of the electrolyte-metallic powder system after the discharging experiments are
334 presented for observation of the reaction products.

335

336 With the use of Fe flakes (Fig. 5A), it appears that electrons are consumed in a reaction where the
337 metallic iron powder oxidizes to iron oxide. Such reaction results in a shorter discharging time,
338 being in this case only 0.25 h in comparison to the 4.4 h needed in the absence of Fe powder (Fig.
339 2A). Some gas evolution on both connecting cables was observed during this experiment, indicating
340 that Fe oxide formation and gas evolution (likely due to water splitting) can occur in parallel.
341 According to the literature, the rusty-colored product on top of the heap of Fe powder (Fig. 5B) is
342 most likely an oxidation product of Fe, likely Fe₂O₃ (Zumdahl and Zumdahl 2000), since the
343 possible sulphites FeS and Fe₂S₃ would be black (Ra and Han 2006). Nie *et al.*, (2015) used some
344 undisclosed type of Fe flakes for the discharge of NiMH batteries, and they also reported a
345 significant decrease of discharge time down to a few minutes instead of hours. Unfortunately, no
346 detailed experimental data was provided in their work to support this claim.

347

348 Discharging with Zn powder in 20% NaCl solution was also considerably faster than without a
349 metallic component (Fig. 6A), reducing the total discharge time from 4.4 h to 0.32 h. The discharge
350 using Zn powder showed at first some gas evolution at the Pt wires, and eventually created a visible

351 solid precipitate, both on top of the metal powder and on the Pt wires. Based on the physical
352 characteristics of the compounds formed, the precipitate is presumed to be Zn(OH)_2 (Zumdahl and
353 Zumdahl 2000). Although a full discharge was possible with Zn flakes, as studied in the preceding
354 Section (3.2), introducing stirring to this system may help prevent deposition of the precipitate on
355 the electrode surface. Overall, the addition of metallic particles showed a major effect on the
356 discharging process. Fe flakes and Zn powder were able to produce a reaction suitable for
357 discharging a LIB significantly faster than in previous experiments, decreasing the discharging time
358 by over 90%.

359

360 The measured discharge time was comparatively longer with Zn powder, even though its particle
361 size is smaller than Fe flakes and consequently offers a higher contact area for the transfer of
362 electrons. It can thus be said that, when using metallic particles, the LIB discharge is more strongly
363 influenced by the type of metallic species rather than its size, at least within the dimensions used in
364 the present study. The effect of sacrificial metal particles with a wider size range will be a scope of
365 a future study.

366

367 **3.4 Direct submersion of the battery in electrolyte solution**

368 Once it was demonstrated that electrochemical discharge using chloride and sulfate solutions is
369 possible, the last experimental stage was to mimic the foreseen industrial preparation process by
370 submerging a fully charged LIB from into salt solution. The experiments were performed using a
371 stagnant 20% NaCl solution. A second experiment was carried out in the presence of metallic
372 particles. In all cases, the connectors on the battery corroded instantly within seconds, hindering the
373 discharging reaction. The corrosion product also blocked the connectors preventing the accurate
374 measurement of voltage in the submerged battery. Examples of the corroded batteries after
375 submersion in the electrolyte solution are shown in [Fig. 7](#). It is interesting to notice that, in the few

376 works presenting experimental results published in the literature (i.e, Lu et al., 2013), it is claimed
377 that a full battery discharge can be obtained after submersion of LIBs into NaCl solutions (1, 5 and
378 10%). Lu et al., (2013) reported that in a concentrated salt solution (i.e., 10%) total discharge
379 occurred in 7 min, even though they explicitly mention damage on the battery casing resulting in
380 leakage of its internal components. Although no clear details on the experimental procedure to
381 measure voltage was offered in such work, it is reasonable to conclude that what was reported was
382 not the electrochemical discharge of the battery in the strict sense, but rather the loss of capacity due
383 to the disintegration of the battery. This would also explain the remarkably fast discharge rates
384 presented in such work. Evidently, corrosion of the battery connectors and leakage is undesired as it
385 leads to uncontrolled chemical changes in the LIB components and contamination of the electrolyte
386 solution. Admittedly, Lu et al., (2013) also reported that using a diluted NaCl solution (i.e., 1%), no
387 corrosion occurred, but the discharge rate decreased to 70 min.

388

389 In order to develop a strategy to prevent the corrosion of the battery poles when batteries are
390 submerged in electrolyte, it is necessary to identify their composition. Only in that way, an
391 electrolyte that could minimize the corrosion of the poles could be potentially found. With that aim,
392 two fully discharged LIB batteries from different manufacturers were dismantled and their
393 connectors analyzed with XRF. As presented in Table 1, there is no consistency in the composition
394 of connector materials. Although the major components of these two LIB connectors are Cu and Ni,
395 they are present in vastly different proportions. The same metals were not always present, as Sn was
396 only detected in one of the battery connector types. Furthermore, the variation in size and shape of
397 connector poles in these two samples reflects the diversity of battery designs in the market.
398 Evidently, this represents a major challenge for the design of robust processes capable of
399 discharging a battery while inhibiting their corrosion.

400 3.5 *Waste Management*

401 As result of the study hereby presented, it has become evident that the current LIB materials have
402 not been designed for bulk discharge or recycling. Considering that there are no uniform standards
403 for the connector materials design or composition, eliminating the corrosion of connector poles
404 during electrochemical discharge upon submersion in electrolyte solutions appears to be a
405 practically impossible task at present. It is thus surprising that, while LIB discharging cannot be
406 performed in practical terms by submerging the batteries in salt solution, this approach has been
407 proposed as a feasible alternative in previous literature (Li et al., 2016; Lu et al. 2013; Zhang et al.
408 2013; Ra and Han 2006; Zang et al. 2013). The current waste management approach for
409 electrochemical discharge of LIB would require a classification, not only on the type of battery, but
410 also on the manufacturer and model, which could be prohibitively expensive. In the search for a
411 practical solution, a new LIB design-for-recycling approach, pairing connector materials with
412 suitable electrolyte solutions would be necessary. This could well be a topic of interest for future
413 research in the area of LIB recycling technologies.

414 4 **Conclusions**

415 This study presented a systematic experimental study aimed at demonstrating whether the idea of
416 electrochemical discharge of LIBs using salt electrolyte solutions is a practical pre-processing step
417 in recycling industries. In *ex-situ* discharge experiments, NaCl proved to be the most effective
418 electrolyte for LIB discharge and increasing its concentration reduced the discharge time down to
419 4.4 h with 20% solution. As the formation of chlorine gas may be a concern, the use of sulphate
420 salts was also explored. The downside of using sulphate salts was the formation of metallic
421 precipitate on the Pt wires that hindered the discharge reaction. Nevertheless, when stirring was
422 introduced to the NaSO₄ solution, the discharge rate was accelerated and the battery was fully
423 drained within 3.1 h.

424

425 With the aim of improving the rate of discharge, fine metallic particles were introduced into the
426 system. Fe flakes provided the fastest discharging reaction but an undesired by-product
427 contaminated the electrolyte solution. For industrial process, the discharge in the presence of
428 metallic particles in a 20 wt% NaCl solution with stirring seems as the most promising option,
429 provided the corrosion of the current connectors can be prevented.

430

431 Indeed, the corrosion of the battery connector poles is the main practical challenge for
432 electrochemical discharge of LIBs, as it leads to incomplete discharge or leakage of internal battery
433 components. This represents a strong limitation to its current implementation in industrial
434 processes, even when other authors seem to have overlooked the implications of this inevitable
435 phenomenon. The results of the present work shed some light into an issue that demands further
436 efforts from the research community. If LIB recycling is to be promoted, perhaps the fabrication
437 standards for LIBs need to be modified, taking into consideration a design-for-recycling philosophy,
438 involving the material composition and physical structure of external components such as casings
439 and connectors.

440

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446

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Figure Captions

Fig. 1. Schematic representation of the experimental setup used to measure voltage of a battery while discharging *ex-situ* with salt solutions: (A) with salt solution only, and (B) with added metallic particles

Fig. 2. LIB discharging curves in aqueous solutions with various concentrations of (A) NaCl, (B) NaSO₄, (C) FeSO₄, and (D) ZnSO₄

Fig. 3. Deposits formed during discharge reactions with different salt solutions: NaCl solution (A), NaSO₄ solution (B), FeSO₄ solution (C) and ZnSO₄ solution (D).

Fig. 4. LIB discharging curves using NaSO₄ solutions with and without stirring

Fig. 5. LIB discharge rate in stagnant NaCl solution (20%) in the presence of Fe flakes (A); a photograph of the precipitates obtained after electrochemical discharge (B).

Fig. 6. LIB discharge rate in stagnant NaCl solution (20%) in the presence of Zn powder (A); a photograph of the reaction setup at the beginning of the experiments (B); a photograph of the reaction products at the end of the discharge (C)

Fig. 7. Corroded LIB connectors after submersion in a 20 % NaCl solution

Table Caption

Table 1. XRF analysis of LIB connectors from two different manufacturers

Table

	Ni	Cu	Fe	Au	Sn	Other
Samsung	8 %	67 %	0 %	2 %	10 %	13 %
Nokia	44 %	30 %	0 %	24 %	0 %	3 %

Figure 1

Figure 2
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