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

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

1 Introduction

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

Batteries in general, and LIBs in particular, have complex material compositions in which valuable metals can be found, such as Cu, Li, Co and Ni (Espinosa et al., 2004; Xu et al., 2008; Georgi-Maschler et al., 2012). There is thus a strong interest on the recovery of such metals (Chen et al., 2017). Rare earth elements (REE) are other interesting materials that can also be found in battery
scrap, as they are considered critical resources due to their high supply risk and economic importance (European Commission, 2014). Furthermore, the collection and recycling of batteries is important not only due to the valuable materials they contain, but also because of their possible negative environmental impact. Under certain conditions, battery scrap can be considered as toxic or hazardous metallic waste (Chen et al., 2011; Zhang et al., 2013) or may contain corrosive and flammable electrolytes (Nan et al., 2006). In addition, under the current recycling practices, battery scrap is often a mixture of different types of batteries such as nickel-metal hydride (NiMH) or nickel-cadmium cells (NiCd) which contain toxic metals, like Cd and Hg (Lund, 2001). For the reasons mentioned above, there are important economic and environmental drivers to develop efficient systems for battery recycling.

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

To minimize the risks during crushing of LIBs, various approaches have been suggested. Some solutions include freezing LIBs with liquid nitrogen before crushing (Li et al., 2010) or processing the batteries in an inert atmosphere, either under vacuum or in the presence of inert gases like Ar or
CO₂ (Lain, 2001; Tedjar et al., 2007). Another option is to crush a limited flow stream of batteries, with the aim of minimizing the impact in the processing plant when some of them explode. All of these approaches are, however, cumbersome, expensive and consume valuable resources (Sonoc et al., 2015). In addition, these practices do not account for the hazardous potential during storage and transportation. Indeed, it is a common practice nowadays to collect and store spent batteries of a mixed composition in a non-organized manner, which results in the risk of short-circuiting due to unwanted contact between batteries or due to possible defects in damaged battery cases. Stored LIBs have been attributed to be the cause of fires in recycling plants, warehouses, and during transportation (Wang et al., 2012). Such fires have been attributed, for example, to accidental short circuiting due to the absence of suitable containers in the presence of water (Lisbona et al., 2011).

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

In previously published literature, several authors have claimed that the electrochemical discharging of batteries in recycling plants is a process well known and commonly used (Li et al., 2016), that it can be performed without major challenges (Ra et al., 2006), is relatively fast (Lu et al., 2013) and
requires easily available resources (Zhang et al., 2013; Zang et al., 2013). Nevertheless, descriptions published in the literature are vague and offer neither evidence on the alleged procedures used, nor details of the specific experimental setups utilized (Lu et al., 2013). Such lack of experimental details raises various questions on the feasibility of electrochemical discharge as a pre-processing step for LIBs recycling in real processes. As discharging appears to be a fundamental step on the pre-processing of LIBs, the work hereby presented focuses on the systematic study of the potential conditions for their electrochemical discharge. To the best of the authors’ knowledge, this is the first critical study of electrochemical discharge of LIBs using salt solutions. The analysis of the discharging behavior of LIBs using different electrolyte solutions, either stagnant or under stirring, and in the presence or absence of sacrificial metal is presented. Based on the experimental results, it is intended to define the potential and limitations on the use of salt electrolytes for LIB discharge, and thus determine whether this is a suitable alternative, as has been previously suggested and, so far, generally accepted. Although it would be useful to expand this study on batteries other than LIBs (with a voltage of ca. 4V), the electric potential in other batteries such as NiMH or alkaline batteries (1.2V and 1.5V, respectively; Linden et al., 2002), is not high enough to produce an efficient discharge reaction. Thus, other battery types are not included in the scope of this work.

2 Experimental methods

The first set of experiments was performed using external Pt wires connected to the poles of the battery and submerged in aqueous salt solution contained in a stirred beaker, thus closing the circuit (Fig. 1A). Pt wires were selected for this study as this metal has a naturally high corrosion resistance and does not take part on the electrochemical reactions. The salt solution in this case acted as a controlled short circuit or as a primitive resistor, discharging the battery. Using this setup, the battery was not placed in direct contact with the electrolyte solution and thus, its physical
integrity was not compromised. Using this approach, it was possible to monitor the evolution of the electrical potential of the LIB due only to electrochemical discharge (i.e., not attributable to physical damage to the battery). This setup allows the study on the discharging potential of the electrolyte solution and its associated kinetics. The battery discharge was monitored by a continuous measurement of voltage using an IviumStat potentiostat (Teamator, Sweeden).

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

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

The salt solutions initially chosen for the experiments were NaCl (Merck, p.a.), NaSO₄ (FF-Chemicals, p.a.), FeSO₄ (Rieder-de Haën p.a.) and ZnSO₄ (J.T. Baker p.a.). The salts were dissolved in ultra-pure, de-ionized water. For each of these salts, solutions with three different
concentrations (5 wt%, 10 wt% and 20 wt%) were produced, the only exception being NaSO₄ since 20% is over its saturation limit and therefore, only 5 and 10% solutions are reported. The aforementioned concentrations were selected for comparison with previously reported data (Lu et al., 2013; Li et al., 2016). These experiments were performed without stirring. In the case of NaSO₄ where no full discharge was obtained with a stagnant solution, stirring was introduced into system with a speed of 600 RPM.

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

The last set of experiments was carried out by submerging the battery samples into the electrolyte solution to simulate the industrial application method suggested by other authors (e.g., Lu et al. 2013) and to observe the effect of corrosion on the battery. Fully charged LIBs were submerged, first into a 20% NaCl solution, and later into solutions with added Fe flakes and Zn powder. These experiments were only performed in 20% NaCl solution since this was the electrolyte offering the fastest discharge, as will be detailed in Section 3. In the case of direct battery submersion,
corrosion in the poles was observed. To get a better understanding of components that can be corroded during discharge, analysis with X-ray fluorescence (XRF) X-MET5000 (by Oxford Instruments) was performed with the aim of gaining insight towards potential improvements in the discharging process or the battery design.

3 Results and discussion

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

\[
\text{Anode: } 2H_2O \rightarrow O_2 + 4e^- + 4H^+ \quad E^0 = 1.23 \text{ V (1)}
\]

\[
\text{Cathode: } 2H^+ + 2e^- \rightarrow H_2 \quad E^0 = 0.00 \text{ V (2)}
\]

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

\[
\text{Anode: } 2\, Cl^- \rightarrow Cl_2 + 2\, e^- \quad E^0 = 1.36 \, V \quad (3)
\]

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: NaSO\(_4\), as it has the same anion than NaCl, as well as FeSO\(_4\) and ZnSO\(_4\) 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.

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

As seen from the profile obtained with NaSO₄ solution (Fig. 2B), the change in the salt anion from chloride to sulfate significantly affected the discharge behavior of LIBs. Not only were longer induction times required, but it was also found that the batteries were only partially discharged with NaSO₄ salt solution, reaching a plateau at around 3 V. Interestingly, the fast formation of a reddish-color precipitate in the solution was observed during these experiments (Fig 3B). It is reasonable to assume that such precipitate blocks the reaction sites at the Pt wires, thus preventing a full battery discharge. The color of the precipitate suggests that it is some type of solid sodium sulfate (Na₂S₅; Steudel 2003), however, detailed analysis was not in the scope of this work. As seen in Fig. 2B, the discharge in NaSO₄ solution initiates after a longer induction time with the higher concentrated
electrolyte (10%) compared with the 5% solution, perhaps due to a faster formation of the precipitate, thus inhibiting the battery discharge. This is a reasonable explanation, as it is well established that the rate of formation of precipitates depends on the salt concentration.

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

\[
\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe(s)} \quad E^0 = 0.41 \text{ V} \quad (4)
\]

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

\[
\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn(s)} \quad E^0 = 0.76 \text{ V} \quad (5)
\]

The formation of metallic Zn is substantiated by the grey hue of the precipitate (Zumdahl and Zumdahl 2000), while the reaction at the other electrode remains as hydrogen evolution (Reaction...
An interesting observation in the case of ZnSO₄ is that no discharge was measured when a 10% solution was used, while a decrease in voltage was observed at both higher (20%) and lower (5%) concentrations. The reason may be associated with the rate of precipitation at the electrodes. Indeed, in the particular case of 10% ZnSO₄ (Fig. 2D), the formation of the solid precipitate was fast, inhibiting the electrochemical reactions even from early stages of the process. Although precipitate formation was also observed at the lower concentration (5 wt%), the growth of Zn precipitate was slower, allowing the discharge of LIBs down to ca. 3 V. On the other hand, with the highly concentrated solution (20%), the voltage drop may have been fast enough to start before the formation of the precipitate, although the plateau was also reached faster due to the eventual formation of precipitate on the Pt wire.

In summary, NaCl provides an efficient media for discharging batteries since it does not result in precipitate formation. None of the sulfate salt solutions was able to entirely discharge the batteries, likely due to precipitate deposition on the Pt connectors. As seen in Fig. 2, in most cases a small decrease in cell voltage was obtained, followed by a sharp drop in the cell voltage or a plateau depending on the salt solution. For all salts solutions, increasing the salt concentration reduced the required discharging time, with the exception of ZnSO₄ at 10%. Nevertheless, since it is not entirely possible to rule out the formation of chlorine gas from the NaCl solutions, a different approach is evaluated in the following Section to use sulfate salt solutions with the aim of eliminating the accumulation of precipitate on the electrode reactive sites.

### 3.2 Discharge in stirred solutions

As mentioned in Section 3.1, it was inferred that the inability of sulfate salt solutions to fully discharge the LIBs was related to the deposition of precipitates on the electrode wires. To study if the discharge can be enhanced by preventing the accumulation of this precipitates (Fig. 2),
discharge experiments using NaSO$_4$ solutions at 5 and 10% were carried out with the aid of a magnetic stirrer rotating at 600 rpm. Interestingly, the discharging rate was significantly improved, as observed in the results presented in Fig. 4.

For comparison, Fig. 4 also presents the results of experiments using NaSO$_4$ electrolyte without stirring. As mentioned in Section 3.1, the discharge reached a plateau around 3 V, attributed to precipitate formation on the Pt wires. However, when stirring is applied, the precipitate was dispersed in the electrolyte solution instead of blocking the wires, thus allowing a full battery discharge. At a concentration of 5%, the decrease in voltage initiates at the same time with and without stirring, but with stirring a full battery discharge is obtained after 9.3 h. For 10% NaSO$_4$ solution, the discharge was completed after 3.1 h with stirring, an even shorter time than in the non-stirred NaCl solution (Fig. 2A). These results clearly support the hypothesis that precipitate deposition on the Pt electrodes is the responsible phenomenon of an inefficient battery discharge.

As was discussed in case of NaSO$_4$ without stirring (Fig. 2B), the rate of precipitate formation is enhanced at higher electrolyte concentrations. However, since stirring prevents deposition of solids on the electrodes, the influence of salt concentrations is analogous to the case with NaCl: with higher concentrations, a faster movement of ions and gas evolution is expected, resulting in a quicker discharge. These results confirm that, in cases where chlorine gas formation cannot be tolerated, it is possible to fully discharge the batteries using NaSO$_4$ solution as an electrolyte, provided deposition of precipitates is prevented, e.g., with stirring.

3.3 Discharge in the presence of metal particles

The second phase of the experimental work hereby presented was to introduce an additional metallic component into the system to provide an additional possibility upon which the energy of a battery can be redirected, potentially accelerating the discharging process. The use of metallic additives in battery discharging processes have been published previously: Nan et al., (2006)
reportedly discharged NiMH batteries in 30 min using water as electrolyte and a substance described as “electric iron powder”, while Nie et al., (2015) used a NaSO₄ solution in the presence of Fe powder to discharge LIBs in 24 h. In the present work, the effect of two different metallic species was studied and they were selected to be the same metals used in the salt solutions (Fe and Zn in the form of flakes and powder, respectively). For the electrolyte, a 20% NaCl solution was selected since it provided the fastest discharge, as discussed in Section 3.1. Fig. 5 and 6 show the discharge curves obtained in the presence of Fe and Zn powders, respectively. In addition, photographs of the electrolyte-metallic powder system after the discharging experiments are presented for observation of the reaction products.

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

Discharging with Zn powder in 20% NaCl solution was also considerably faster than without a metallic component (Fig. 6A), reducing the total discharge time from 4.4 h to 0.32 h. The discharge using Zn powder showed at first some gas evolution at the Pt wires, and eventually created a visible
solid precipitate, both on top of the metal powder and on the Pt wires. Based on the physical characteristics of the compounds formed, the precipitate is presumed to be Zn(OH)$_2$ (Zumdahl and Zumdahl 2000). Although a full discharge was possible with Zn flakes, as studied in the preceding Section (3.2), introducing stirring to this system may help prevent deposition of the precipitate on the electrode surface. Overall, the addition of metallic particles showed a major effect on the discharging process. Fe flakes and Zn powder were able to produce a reaction suitable for discharging a LIB significantly faster than in previous experiments, decreasing the discharging time by over 90%.

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

### 3.4 Direct submersion of the battery in electrolyte solution

Once it was demonstrated that electrochemical discharge using chloride and sulfate solutions is possible, the last experimental stage was to mimic the foreseen industrial preparation process by submerging a fully charged LIB from into salt solution. The experiments were performed using a stagnant 20% NaCl solution. A second experiment was carried out in the presence of metallic particles. In all cases, the connectors on the battery corroded instantly within seconds, hindering the discharging reaction. The corrosion product also blocked the connectors preventing the accurate measurement of voltage in the submerged battery. Examples of the corroded batteries after submersion in the electrolyte solution are shown in Fig. 7. It is interesting to notice that, in the few
works presenting experimental results published in the literature (i.e., Lu et al., 2013), it is claimed that a full battery discharge can be obtained after submersion of LIBs into NaCl solutions (1, 5 and 10%). Lu et al., (2013) reported that in a concentrated salt solution (i.e., 10%) total discharge occurred in 7 min, even though they explicitly mention damage on the battery casing resulting in leakage of its internal components. Although no clear details on the experimental procedure to measure voltage was offered in such work, it is reasonable to conclude that what was reported was not the electrochemical discharge of the battery in the strict sense, but rather the loss of capacity due to the disintegration of the battery. This would also explain the remarkably fast discharge rates presented in such work. Evidently, corrosion of the battery connectors and leakage is undesired as it leads to uncontrolled chemical changes in the LIB components and contamination of the electrolyte solution. Admittedly, Lu et al., (2013) also reported that using a diluted NaCl solution (i.e., 1%), no corrosion occurred, but the discharge rate decreased to 70 min.

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

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

4 Conclusions

This study presented a systematic experimental study aimed at demonstrating whether the idea of electrochemical discharge of LIBs using salt electrolyte solutions is a practical pre-processing step in recycling industries. In ex-situ discharge experiments, NaCl proved to be the most effective electrolyte for LIB discharge and increasing its concentration reduced the discharge time down to 4.4 h with 20% solution. As the formation of chlorine gas may be a concern, the use of sulphate salts was also explored. The downside of using sulphate salts was the formation of metallic precipitate on the Pt wires that hindered the discharge reaction. Nevertheless, when stirring was introduced to the NaSO₄ solution, the discharge rate was accelerated and the battery was fully drained within 3.1 h.
With the aim of improving the rate of discharge, fine metallic particles were introduced into the system. Fe flakes provided the fastest discharging reaction but an undesired by-product contaminated the electrolyte solution. For industrial process, the discharge in the presence of metallic particles in a 20 wt% NaCl solution with stirring seems as the most promising option, provided the corrosion of the current connectors can be prevented.

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

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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>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cu</th>
<th>Fe</th>
<th>Au</th>
<th>Sn</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samsung</td>
<td>8 %</td>
<td>67 %</td>
<td>0 %</td>
<td>2 %</td>
<td>10 %</td>
<td>13 %</td>
</tr>
<tr>
<td>Nokia</td>
<td>44 %</td>
<td>30 %</td>
<td>0 %</td>
<td>24 %</td>
<td>0 %</td>
<td>3 %</td>
</tr>
</tbody>
</table>
Figure 1

A: LiB in a salt solution

B: LiB in a salt solution with Zn or Fe powder
Figure 2

Battery voltage vs. Time for different concentrations of NaCl, NaSO₄, FeSO₄, and ZnSO₄.