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Voltage behavior in lithium-ion batteries after electrochemical discharge and its implications on the safety of recycling processes



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ABSTRACT

The demand of lithium-ion batteries (LIBs) is exponentially increasing, largely due to the ongoing transition towards electric transportation. To support the raw material supply for LIB manufacturing, there are significant ongoing efforts to recycle battery materials. Nevertheless, end-of-life LIBs entering recycling processes may still contain remnant energy, representing a potential hazard during handling and processing. Despite the urgency to improve LIB recycling, there is a lack of serious discussion in the literature regarding discharging strategies for LIBs. The electrochemical discharge using aqueous salt solutions route for example, has been widely mentioned without proper evidence of its usefulness. Among the discharge phenomena so far overlooked is the voltage recovery effect of batteries (a.k.a. voltage rebound/relaxation), where battery power appears to spontaneously surge, even after readings of full discharge in a circuit. In this work, a systematic study on the behaviour of LIBs during discharge in aqueous salt solutions is presented to better understand this unit process, addressing the challenges to fully drain energy from spent batteries prior to recycling. We demonstrate that the voltage recovery effect creates false readings for the battery charge level that represent risks during processing. If electrochemical discharge is employed, we present a methodology to decrease open circuit voltage in aqueous salt solution to 2.0 V, suitable for mechanical processing.

Introduction

Lithium-ion batteries (LIB) are all around us: they are in our pockets, in our backpacks, in our household equipment, in our cars and in our solar panel systems. There is a massive global demand for LIBs and according to some estimates, their production volume is roughly doubling every five years [1]. The energy stored in LIBs has grown from 45 GWh in 2015 to 125 GWh in 2020, and it is forecasted to reach 390 GWh by 2030 [1]. This will inevitably be associated with an increasing number of spent LIBs, requiring efficient and safe recycling technologies. Current LIBs contain valuable elements such as Cu, Al, Co and Li, depending on the battery chemistry. Particularly, Co and Li reserves are limited (Li 13 Mt (2013), Co 7.5 Gt (2012)) [2] and so, the recovery of valuable materials in existing batteries will soon be essential. In addition, the mining of metals is an energy-intensive activity with high ecological and societal impact [3]. In Europe alone, the LIB market reported a total of 65, 500 tons of LIBs consumed between the years 2013-2014 [4], while only about 1900 tons were recycled in the same time frame. It is known that the improper disposal of batteries to landfills is the single most important reason for heavy metal contamination of soil [5].

One of the often-overlooked challenge of State-of-the-Art recycling technologies is the need for reliable, fast and cost-efficient solutions to ensure the safe discharge of the waste battery piles [6]. In fact, already during the collecting, storing and transportation stages, LIB waste is a potential fire hazard that can further prevent logistic actors from investing in recycling LIBs. Particularly, the organic electrolyte reacts with atmospheric molecules to produce harmful toxic vapours during the recycling process [7], making LIB recycling rather unappealing [8]. The current volumes of LIBs have allowed this unsafe practice to continue in recycling facilities, but the aforementioned increase in waste LIBs will result in quantities where fire hazard due to residual charge in batteries become a serious risk.

There are currently two main routes to recycle LIBs and recover valuable elements: the mechanical and the pyrometallurgical route [9, 10]. In the direct pyrometallurgical route – the batteries are processed in a high-temperature metallurgical process regardless of their State of

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Received 26 October 2020; Received in revised form 8 January 2021; Accepted 19 January 2021 Available online 25 January 2021 2352-152X/© 2021 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). Charge (SOC). This route, however, only provides the possibility to recover some of the LIB materials. For instance, in rotary kilns treating LIBs, only metallic components such as Cu, Al and Co are recovered while all other components (e.g., Li, graphite and plastics) are lost [11]. Therefore, the sole utilization of such high-temperature route provides limited benefits from an overall raw materials perspective. To improve the recovery of materials, it has been recently proposed the use of mechanical pre-concentration to generate additional material streams [12, 13]. These individual streams can be subsequently processed to ensure the highest material recovery by hydrometallurgical [14,15] or pyrometallurgical steps [7,13]. According to the literature, such pre-processing allows the recovery of Li through hydrometallurgical technologies, currently under development [16,17]. However, mechanical recycling presents some hazards as it invariably requires crushing or dismantling of LIB cells for material liberation. As the active components of LIBs with remnant charge are liberated during crushing, they short circuit causing violent explosions, representing a risk for equipment and personnel alike. To avoid such hazards, SOC should preferably be less than 2 % [18], and optimally below 0 % (corresponding to a voltage below 2 V) [19]. Currently, there are no requirements to discharge batteries prior to recycling, and the preferred practice is to slowly feed LIBs into the crushing stage to withstand the violent release of energy.

To enhance the mechanical recycling stages and ensure safe handling of the battery waste, efficient and robust LIB discharge methods are needed. A conventional method for battery discharge is connecting individual batteries to resistors. Such approach may be reasonably applied for large battery backs (such the ones found in electric vehicles), but for commonly used cells used in electronic devices, lacking standard size or geometries, a manual connection to resistors is not an economically viable option. Finally, the current of the electrical circuit should be monitored carefully in order to reduce the risk of fire [20]. Upon a review in the scientific literature related to battery recycling, it was found that prior to 2017, the electrochemical discharge of LIBs was described only in general terms as it being performed by submersion in aqueous salt solutions, with NaCl or Na₂SO₄ typically mentioned [21-27]. However, no experimental data or detailed procedure was offered to validate this statement. The most alarming aspect is that, according to the most recent literature, the use of salt solutions for LIB discharge remains accepted without serious critical evaluation [10]. For that reason, our research group recently carried out a systematic study of electrochemical discharge of LIBs, where a rapid corrosion of the connector poles in various aqueous salt solutions was observed [28]. These findings have been since confirmed independently by two other research groups [29,20]. Such fast corrosion, particularly in NaCl solutions, inhibits the full charge transfer from the battery to the solution, thus limiting the discharge of batteries to acceptable levels. The work by Shaw-Stewart et al. [29], investigated the effect of different salt solutions on pole corrosion and rate of discharge. According to their work, the lowest corrosion for LIB poles was documented with carbonate salts: Na₂CO₃ and K₂CO₃ making them a reasonable choice as discharge medium.

Later, Nembhard [20] tested discharging with various salt species but continued monitoring the battery voltage after being removed from the solution, reporting a voltage recovery of up to 2.5 V. The phenomenon of voltage increase after the battery is removed from a circuit is well documented in other contexts and is called "voltage rebound" in electrical engineering and "voltage relaxation" in electrochemistry. For simplicity, it will be called "voltage recovery" in this work. Although voltage recovery has been documented for decades, it is not widely studied [30,31]. In electrical engineering, the study of voltage recovery has focused on exploiting this phenomenon to increase the battery operation lifetime [32,33]. From the electrochemical perspective, its study is usually connected to the activation or the concentration overpotential in the cell and is studied mainly in voltage ranges above 2.5 V (> 0% SOC) to aid on the State of Health (SOH) analysis of batteries [34]. Also, studies of deep discharge to lower SOCs have been conducted, but they focus on its influence on battery lifetime and the damage to the cell materials [35]. On the other hand, at the end-of-life conditions, the operational mechanism in the cell is no longer relevant, and the focus should shift to the safe withdrawal of energy and the quality of elements to be subsequently recovered. The studies on voltage recovery effect show that, after disconnection from the external current circuit, the extent of recovery depends on both temperature and LIB electrode material [36]. Nevertheless, very little interest has been presented on LIB discharge below 0 % SOC and how the voltage recovery effect influences the recycling processes. This represents an additional risk that has not yet been considered in the electrochemical discharge route for LIBs. Indeed, voltage relaxation misrepresents the SOC, as the battery contains residual energy even though voltage readings suggest the contrary.

Typically, the internal state of charge is measured by the difference in potential between two poles (negative and positive). Nevertheless, this information does not separate attributes from the electrodes and therefore does not contain detailed information of the phenomena occurring in the cell [36], nor does the voltage explicitly distinguish attributes from simultaneously occurring mass transfer mechanisms such as Li-ion transfer in the liquid electrolyte or in the solid porous electrode material. It should be kept in mind that LIBs are complex electrochemical systems. It is generally accepted that the battery is charged by pushing electrons to the cell, which is compensated by the re-positioning of positive Li-ions to the negative electrode. Discharging occurs when electrons flow out of the cell and the Li-ions move back into the positive electrode, as schematically presented in Figure 1. In summary, there are two simultaneous phenomena preventing the proper evaluation of the SOC of LIBs during electrochemical discharge: i) corrosion of connecting poles; and ii) voltage relaxation.

If electrochemical discharge is going to be exploited in future LIB recycling processes, we need to understand how this step can be performed and evaluated in a safe and controlled manner. The aim of this work is to further study the LIB battery voltage behaviour after discharge in salt solutions and to find possible process conditions that would ensure safety for battery handling prior to mechanical processing. The studies are conducted with two different commercial battery types (with or without discharge protective circuit) in aqueous solutions of two carbonate salt species that previously reported low corrosion rate [28]. It is expected that this work will contribute to a methodical and scientific discussion on the field of electrochemical discharge of LIBs and LIB recycling.



Figure 1. LIB cell schematic and the ion movement at the case of discharge.

Materials and methods

The batteries used in this work were Panasonic Cameron Sino CS-NCR18650B (China, capacity 3250 mAh) containing LiNiCoAlO₂ cathode (NCA) without any protective circuit and commercial 18650-type cylindrical LIB cells, Biltema ICR18650 (Sweeden, capacity 2950 mAh) with a LiCoO₂ cathode (LCO) and a protective circuit, shown in Figure 2 A-B, respectively. The protective circuit is an electronic circuit integrated into the cell packaging whose aim is to prevent the battery to be charged or discharged too rapidly and to reach very high/low SOC values. To ensure repeatability, new batteries were used for each experiment in this study. Both batteries had a reported nominal voltage of 3.7 V and maximum voltage of 4.2 V. Additionally, the Panasonic batteries had junction plates at terminals (Figure 2B) which increases the conductive area of the terminals and might affect the battery discharge rate.

Aqueous salt solutions were prepared using 5 or 10 wt% Na₂CO₃ (VWR, 99.9 %) or K₂CO₃ (Sigma-Aldrich, 99.5 %) salts and de-ionized water ($<0.5 \ \mu S \ cm^{-2}$). These salt species were selected as they showed low corrosion effect in a previous study [28]. Batteries were submerged into a glass beaker containing the salt solutions using an in-house built battery holder (Figure 2C) that enabled lifting of the battery in a rapid and efficient way. Due to the length of some experiments, water evaporation was occasionally detected. Thus, to maintain a constant concentration, additional de-ionized water was added regularly to maintain a constant volume. To measure voltage, the battery holder was lifted from the salt solution, the battery poles were rinsed with de-ionized water and dried to obtain reliable voltage reading with a voltmeter (Biltema, Art.15-124). This voltage is considered as the potential at close circuit voltage (E_{CCV}), even though small changes in voltage can occur between the removal of the cell from the solution and measuring. A few seconds after removal from the salt solution, the measured battery voltage typically increased around 10 mV than that at the closed circuit. If the voltage had changed more than 1 mV, the battery was submerged back to the solution and measured again after an hour. Once voltage remained constant, the battery was kept out of the electrolyte solution and the voltage was monitored further as the open circuit voltage (E_{OCV}), corresponding to the potential difference between the poles and the energy remaining in the battery. Additionally, all the batteries were visually inspected for corrosion and photographed to document changes in their external structure.

During the discharge in the aqueous salt solution, it was observed that gaseous products were formed at both connecting poles. Since the amount of gas produced was very small, these gaseous products could not be analysed with the current setup. It is however reasonable to assume that the energy from the battery is consumed by the water splitting reaction where water breaks to hydrogen and oxygen gases. The observation that the voltage during LIB discharge was never below 1.7 V further supports this explanation, since water splitting has a voltage of



Figure 2. (A) Panasonic battery with junction plates at the terminals, (B) Biltema battery, (C) The in-house battery holder used for the experiments.

around 1.7-1.9 V in practice [38]. Thus, most likely hydrogen gas is formed at the cathode and oxygen at the anode. As carbonate salts were used, we cannot exclude the possibility of CO_2 formation, but the possible evolution of CO_2 did not require additional safety measures as the experiments were performed in a fume cabinet. The collection and characterization of gas products is certainly interesting and will likely be carried out in future studies.

Results and Discussion

Prior to mechanical recycling, it is vital to know the exact voltage of end-of-life batteries called open circuit voltage (E_{OCV}) in order to ensure a safe handling. Currently, the only possibility is to measure LIB voltage between the poles, determining the potential between anode and cathode. Therefore, it is important to fully understand when and how to carry out reliable voltage readings. Several studies show that LIB voltage can be decreased in aqueous salt solutions close to a 1.7 V limit, measured directly after removal from the solution. As mentioned above, this procedure overlooks voltage recovery and may result in the misinterpretation of the battery SOC.

For the reasons mentioned above, the LIB voltage evolution was monitored during submersion in an aqueous salt solution, but also after removal. Additionally, we studied the voltage recovery phenomena that occurs with fast battery discharge and its effect on LIB voltage changes during the possible dead time prior to mechanical processing. To that aim, this study is divided into two different sub chapters: first, we observe the effect of battery type and electrolyte salts and their concentration on the first discharge–voltage recovery cycle. Secondly, the effect of sequential discharge cycles in aqueous salt solutions and the possibility to further reduce the battery voltage is presented.

3.1. Single discharge cycle

The voltage evolution during a single discharge–voltage recovery cycle for both battery types using two different aqueous salt solutions is presented in Figure 3. As seen, the Biltema batteries discharge ended around 72 h and Panasonic batteries discharge ended around 95 h. It should be mentioned that two repetitions were performed for each experiment, but the results did not exhibit any measurable variation.

Figure 3 shows that the battery type has a stronger influence on the voltage behaviour than the type of carbonate salt in the electrolyte solution. In Panasonic batteries, the voltage initiates from higher value, but the discharge is more rapid and falls to lower values in comparison



Figure 3. Voltage evolution of LIB during discharge in salt solutions and afterward voltage recovery effect in air for Biltema (discharge ended at 72 h) and Panasonic batteries (discharge ended at 95 h).

to Biltema batteries, which barely reached voltages below 2.0 V. This could be due to the protection circuit preventing an uncontrolled, fast discharge in the latter. When batteries are designed, their safety must be a main design criterion, and it is interesting to observe the impact that these measures have on the products recyclability.

Figure 3 also shows that it takes around 20 h longer for the Panasonic batteries to reach a steady E_{CCV} , but also the voltage rebound is only to 2.3 V, comparatively lower than with the Biltema batteries (2.6 V). Both findings are in line with the voltage recovery effect reported by Nembhard [20]. As seen, under no circumstances was a voltage lower than 1.8 V obtained, as the likely electrochemical reaction consuming the electrons is water splitting [39]. After the batteries are taken out from the solution, their E_{OCV} increased in all cases around 0.6 V. This behaviour alarmingly demonstrates that the real cell voltage E_{OCV} does not correspond to the measured voltage directly after removal from a closed circuit (in this case, the electrolyte solution). This is a finding that has not been discussed before in this context and one that represents a serious hazard in recycling facilities.

As the differences between the two salt types were minor, Na_2CO_3 was selected for the following experiments. Subsequently, the effect of salt concentration on the discharge rate was tested using Na_2CO_3 solution at concentrations of 5 and 10 wt%. For the sake of representativity, measurements were conducted on two different batteries. As seen in Fig. 4, more concentrated solutions increased the discharge rate of the battery at the beginning, but the difference has little practical meaning as the lowest voltage was not reached significantly earlier.

Nevertheless, Figure 4 also suggests that an advantage of higher salt concentrations is a slightly lower voltage after recovery. In a previous work, the battery discharge was also found to be faster with higher salt concentrations, without a significant difference on the voltage recovery rate or the final voltage level (E_{OCV}) [20]. Unfortunately, the E_{OCV} measured after stabilization (i.e., 2.3 V) is still too high for mechanical recycling. According to these findings, the recovery effect seems not dependent on the properties of the discharging solutions, but rather on the ion movement inside the battery itself. During these studies with various repetitions, we found that one Panasonic type battery experienced corrosion and this data has been reported elsewhere [39]. This leads to highlight that the battery material casing, even from the same batch, vary in their metal alloying and therefore the risk for casing corrosion is always present at aqueous-salt solutions.

3.2. Sequential discharge in salt solution

4.0

3.5

As was observed in the previous section, the measured voltage after

5 wt% Na₂CO₃

10 wt% Na₂CO₃

10 wt% Na₂CO₃ repetition



the battery was removed from the discharging solution has the possibility to relax back to a higher value. As controlled discharging is important for safe mechanical crushing, this phenomenon needs to be analysed in more detail. It was thus decided to carry out a sequential discharge by reintroducing the batteries into the salt solution after their voltage recovery effect. The results of this sequential discharge-voltage recovery cycles are presented in Figure 5.

Figure 5 shows that the two commercial LIBs hereby studied behaved similarly: the measured voltage of the LIB during the first discharge reached down to 1.95 V close circuit voltage E_{CCV} (orange background), but when removed from to the electrolyte solution (green background), the voltage increased up to 2.6-2.7 V (ca. 750 mV higher than E_{CCV}). It should be noted that, according to these results, a voltage measured directly after discharge would give a false indication that the battery can be treated mechanically with low risk.

When voltage over 2.6 V or constant voltage was obtained, the battery was submerged again in the salt solutions for further extraction of energy (orange background sections in Figure 5). As more bubbles started forming due to water splitting, more electrons were withdrawn from the cell and the measured E_{CCV} dropped back to around 1.9 V. When the LIB was removed from the electrolyte a second time, the battery voltage EOCV increased only to 2.3 V. A similar behaviour was obtained with subsequent cycles, with the lowest measured E_{CCV} and E_{OCV} decreasing with each discharge-recovery cycle. However, voltage recovery was invariably detected, and the voltage always remained above 1.7 V, likely due to the limit for the water splitting reaction [37]. Figure 5 shows that it was possible to obtain E_{OCV} level around 2.0 V with the Biltema battery, which is low enough for safe shredding of LIBs [19], although this took almost 900 h. Overall, it is evident that the protective circuit in a LIB system will not have a strong effect on the LIB discharge. These results demonstrate an urgent need for a model to represent more accurately the relationship between the voltage measured during close circuit (E_{CCV}), the open circuit (E_{OCV}) and the real SOC in the battery.

Considering the long times required for discharge discussed above and the strategic possibility that LIBs spend days in recycling facilities waiting for processing, a discharge period over 300 h was performed in a Panasonic battery. In Figure 6, the voltage of the battery submerged for 2 weeks is presented (light blue dots). For comparison, the behaviour of the Panasonic battery described in Fig 5 is included. As seen, after a discharge over 2-weeks, a recovery effect was still observed, although somewhat lower than during discharge-recovery cycling (dark blue dots In Fig 6). From the experimental data in Figure 6, two independent



Figure 5. LIB voltage behaviour in 5 wt% Na_2CO_3 solution for commercial LIB batteries (Biltema and Panasonic) at various discharge-voltage recovery effect cycles (red background shows the close circuit discharge stages and green the open circuit stages).



Figure 6. Two Panasonic batteries 5 wt% Na_2CO_3 solution: the first one was kept in the solution for 340 h and only removed for voltage measurements. The second was operated as in Figure 5. Trend lines for the closed-circuit voltage, (E_{CCV}) and the open-circuit voltage (E_{OCV}) are based on measured points and provided as a guide for the eye.

trends for E_{CCV} and E_{OCV} states of the battery were constructed. The area between these two lines represents a SOC hysteresis with a magnitude of ca. 500 mV throughout the experiment. As seen, even after 2 weeks in the discharging solution, the measured voltage E_{CCV} can be 1.7 V, whereas the corresponding E_{OCV} is 2.1 V, still high enough to be considered hazardous.

In order to understand the observed behavior of LIBs and design suitable discharging strategies, one can represent rechargeable batteries using the circuit in Figure 7, where the open-circuit voltage of the battery is a function of the state of charge (z(t)). The current of the battery is i(t), which is positive on discharge and is negative on charge. The open-circuit voltage is higher than the terminal's voltage (v(t)) on discharge and lower than the terminal's voltage when the cell is being recharged. In this model, R_0 is added to represent the internal resistance of the battery, a term that also explains the energy inefficiency in the cell, since power will be dissipated by such internal resistance. R_0 is thus responsible for the sudden jump in the voltage level of the battery when the battery is removed from the solution, for example after around 70 h, as it can be seen in Figure 6. $i(t) \times R_0$ is the term that can model the instantaneous response to a sudden change in the current value.

Based on Figure 6, after a sudden increase in the value of voltage, the voltage of the battery increased toward a steady-state value that is caused by slow diffusion processes in the cell. One or more Resistance-Capacitance (RC) networks can be added to the circuit to model the dynamic behavior of the battery. RC networks are used to show the diffusion process in the electrolyte. With a larger number of RC elements, the accuracy of the electrical equivalent circuit of the battery model will be increased but it also leads to a more complex circuit. In the equivalent circuit, R_1 and C_1 are the equivalent polarization resistance and polarization capacitance, respectively. It is worth noting that the voltage of the capacitor cannot change abruptly. The time needed for a completely discharged capacitor to charge around 62.3 % of its final



voltage value is called the time constant of the capacitor (τ). The time constant is a function of the size of the capacitor and the resistance in the RC network. The terminal voltage of the battery is thus approximated with Equation (1). Finally, based on Figure 6, for the 5 wt% Na₂CO₃ solution with pulsed discharge, the first recovery voltage started when the battery had been removed from the solution (almost after 70 h) and converged to its final value (steady-state value) around 160 h after the start of the measurement. Based on the circuit theory, for the practical purposes, we can suppose that the voltage of the RC element reaches its steady-state value after around 4-time constant ($\tau = R_1C_1$) of the RC network. Equation (2) is the approximated time that the battery can find its steady-state voltage [40].

$$v(t) = OCV(z(t)) - v_{C1}(t) - v_{R0}(t)$$
(1)

$$\Delta t \approx 4\tau = 4R_1C_1 \tag{2}$$

There are only few studies that directly focus on the LIB voltage recovery effect. For instance, D. Hauck et al. [19] have shown that LIB voltage recovery effect is dependent on the discharge temperature when the cells are discharged by external load. They discharged the cell at temperatures of -20 and + 40 °C and noticed that the voltage recovery effect (voltage relaxation) initiates slowest with the battery discharged at cold temperature. This study concludes that the voltage recovery effect is the function of the discharge temperature that affect the electrolyte viscosity. At low temperatures, electrolyte viscosity is higher and therefore, the ion conductivity inside the cell is more sluggish. The results at different discharge solutions (Figure 4) confirmed that voltage recovery effect is mainly dependent on ion movement inside the battery and not due to ionic conductivity of the discharge solution. It has also been proposed that the type of LIB cathode material will influence the recovery effect due to differences of Li⁺ ion positioning within these materials [34]. This study included two separate LIB chemistries (i.e., LCO and NCA) which showed little difference in their discharge behaviour. For that, we can conclude that more significant differences in the layered structure chemistry are needed to have a measurable impact on the recovery effect. However, as new chemistries are developed and commercialized, this may be considered as a design parameter for new batteries.

Overall, the recovery effect and consequently, the incomplete battery discharge, cannot be prevented by the type or concentration of electrolyte salt solution. It is thus challenging to find a salt solution system that could discharge the LIB down to a level where no rebound above 2 V is obtained. The results here presented demonstrate the importance to better understand the discharge behaviour of batteries and how it can be influenced to guarantee safe LIB handling for an efficient material recovery.

Conclusion

In order to lower the environmental impact of LIB, their raw materials need to be recovered by efficient LIB battery recycling process. This requires fast, cost-efficient and safe LIB discharge process to minimize the risk of fire and explosion in recycling facilities. Currently, some oversimplified solutions for electrochemical discharge of LIBs have been mentioned in the literature without adequate supporting evidence. For this reason, it is vital that battery discharge experiments in aqueous salt solutions are carried out in a systematic manner. As batteries are not typically studied at low or negative SOC conditions, their discharge behaviour is not properly understood, despite this being vital information for the safe handling of batteries in the recycling processes. In this work we demonstrate that the LIB discharge behaviour presents risks associated with false voltage readings.

Firstly, voltage recovery after electrochemical discharge in salt solutions and its associated misrepresentation of the actual SOC is a phenomenon that has been overlooked in the current LIB recycling literature. If the batteries are just discharged in aqueous salt solution and their voltage measured directly after that, the measured voltage does not correspond to the energy stored in the battery cell. This represents a safety risk during their handling and processing that has been ignored so far, to the best of the authors' knowledge. On the other hand, discharging in aqueous salt solution can leads to corrosion in the batteries randomly.

As it would be possible at the recycling centre to keep the batteries submerged in the solution for a longer time or even cycle the batteries at close and open circuits, the batteries were reintroduced into aqueous salt solution to further withdraw energy after voltage recovery. With this approach a 2 V open circuit voltage with Biltema battery was reached, however after almost two weeks of time. This is a significantly longer time reported in other works where the voltage is read without acknowledging the possibility of recovery. The sequential cycling also provided possibility to remove some of the energy stored into the inner energy storage in the battery and was able to reduce the E_{OCV} level closer to safe battery handling. Keeping the battery for longer time periods in the solution might be one option for safe handling of LIBs at the industrial recycling facilities.

More importantly, this study provides new input for understanding the effect of discharging to negative SOC levels and how it will reflect to voltage behaviour. In line with the findings of previous studies, this work shows that the voltage recovery effect is more related to the ion movement within the battery cell than on the properties of the discharge medium and therefore, further understanding of phenomena occurring inside batteries at low SOC level should be emphasized for the development of recycling technologies. If electrochemical discharge will be used as a unit process in LIB recycling, it is thus important to acknowledge the voltage recovery phenomenon for the design of efficient and safe battery discharging strategies.

CRediT authorship contribution statement

Hassan Rouhi: Formal analysis, Visualization, Writing - original draft. Eero Karola: Investigation, Formal analysis, Visualization, Writing - original draft. Rodrigo Serna-Guerrero: Conceptualization, Investigation, Funding acquisition, Writing - review & editing. Annukka Santasalo-Aarnio: Conceptualization, Investigation, Funding acquisition, Visualization, Writing - original draft.

Declaration of Competing Interest

There are no conflicts to declare.

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