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

Severi Ojanen, Mari Lundström, Annukka Santasalo-Aarnio*, Rodrigo Serna-Guerrero

Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, P.O. Box 16200, 00076 Aalto, Finland

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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, Na₂SO₄, 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.

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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 (Fulleton, 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

* Corresponding author.

E-mail address: annukka.santasalo@aalto.fi (A. Santasalo-Aarnio).

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 and Reddy, 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 pro-

cesses. 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. 4 V), the electric potential in other batteries such as NiMH or alkaline batteries (1.2 V and 1.5 V, respectively; Linden and Reddy, 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, Sweden).

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

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