Waste Management xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Multistage leaching of metals from spent lithium ion battery waste using electrochemically generated acidic lixiviant

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ARTICLE INFO

Article history:
Received 6 September 2017
Revised 21 December 2017
Accepted 29 December 2017
Available online xxxx

Keywords:
Leaching
Resource recovery
Metals
Lithium ion battery
Electrochemistry
Waste

ABSTRACT

Lithium ion battery (LIB) waste contains significant valuable resources that could be recovered and reused to manufacture new products. This study aimed to develop an alternative process for extracting metals from LIB waste using acidic solutions generated by electrolysis for leaching. Results showed that solutions generated by electrolysis of 0.5 M NaCl at 8 V with graphite or mixed metal oxide (MMO) electrodes were weakly acidic and leach yields obtained under single stage (batch) leaching were poor (<10%). This was due to the highly acid-consuming nature of the battery waste. Multistage leaching with the graphite electrolyte solution improved leach yields overall, but the electrodes corroded over time. Though yields obtained with both electrolyte leach solutions were low when compared to the 4 M HCl control, there still remains potential to optimise the conditions for the generation of the acidic anolyte solution and the solubilisation of valuable metals from the LIB waste. A preliminary value proposition indicated that the process has the potential to be economically feasible if leach yields can be improved, especially based on the value of recoverable cobalt and lithium.

1. Introduction

Rapid development, short life span and increased usage of information technology, have resulted in a serious waste management issue surrounding the production, collection and recycling of waste electrical and electronic equipment (WEEE). This unique and inherently complex waste stream is now considered as one of the fastest growing waste streams of the modern era (Zeng and Li, 2014), with the global volume of WEEE generated increasing yearly by 5–10% (Sthiannopkao and Wong, 2013). Lithium ion battery (LIB) waste is an emerging subset of WEEE, which has become the focus of much research for the recovery of valuable metal and reduction of human and environmental health risks associated with their disposal (Pagnanelli et al., 2016).

The management of LIB waste has two primary aims:

(1) Stabilisation of toxic elements and reduction of pressure on land resources to reduce environmental impacts associated with the disposal of LIB waste on human and environmental health; and,
(2) Recovery of valuable and critical elements such as cobalt and lithium from LIB waste to supplement the primary resources that are required for the manufacture of LIBs.

Due to the consumption and loss of these valuable elements and high proportions of metal value contained within the waste when compared to primary virgin mineral resources, LIB waste is now considered a valuable secondary resource and a prime candidate for urban mining (Ongondo et al., 2015). This is especially true in a time where availability of high grade, economically viable and ethically mined mineral resources are declining and mineral processing is shifting to more sustainable methods and technologies (Ongondo, et al., 2015; Sommer et al., 2015; Mudd, 2009).

In Australia, LIBs are not currently categorised as hazardous waste, although they are considered to possess significant safety, human and environmental health risks (Randell, 2016). In addition, there are currently no legislative requirements to promote or enforce the take back or recycling of batteries by manufacturers

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https://doi.org/10.1016/j.wasman.2017.12.033
0956-053X/© 2017 Published by Elsevier Ltd.

Please cite this article in press as: Boxall, N.J., et al. Multistage leaching of metals from spent lithium ion battery waste using electrochemically generated acidic lixiviant. Waste Management (2018), https://doi.org/10.1016/j.wasman.2017.12.033

and distributers, with the major recycling programs focussed on voluntary return by the consumer (Lewis, 2016). A report commissioned to track the generation, fate and infrastructure capacity for the treatment of hazardous wastes in Australia (including LIB waste even though it is not classified as a hazardous waste) indicated that Australia was lacking in specific LIB collection, transport or treatment infrastructure. Therefore, Australia is currently relying on the collection and separation of mixed battery types and sending them overseas for recycling and will be unable to efficiently manage and export this particular waste stream when LIB waste increases to a critical volume (estimated to be in *ca.* 2030) (Randell, 2015).

Approximately 3,000 tons of LIB waste was produced in Australia in 2016 (Randell, 2016). In 2014, it was estimated that less than 2% of the LIB generated was recycled for the recovery of valuable materials (O'Farrell et al., 2014), with the majority of LIB waste being disposed to landfill or stockpiled. There is only one pilot-scale recycling facility designed to specifically recycle LIB in Australia, located in the state of Victoria. There, LIB waste is sorted and broken down into major components such as aluminium foil and copper, plastics and cathodic dust (Lewis, 2016). However, the cathodic dust which contains valuable cobalt, nickel and lithium is exported to countries such as Korea for hydrometallurgical recovery of metals (Randell, 2016; Lewis, 2016).

Recovery of metals from LIB waste has thus far focussed on the application of traditional mineral processing technologies such as hydrometallurgy or pyrometallurgy to recover metals from spent LIB with mixed results (Pagnanelli et al. 2016; Meshram et al., 2015a; Zeng and Li, 2014). Often, the processes that have been most successful require high energy and reagent inputs whilst also producing toxic end products or wastes (such as off gases containing dioxins and furans, or acidic metal-containing effluents) that require further processing before environmental release.

In response to the gap in battery recycling infrastructure and technology in Australia, this research investigated the applicability and feasibility of alternative processes for the recovery of metals from LIB waste. The aim of this study was to develop a suitable process for extracting metals from LIB waste using the following process components:

(1) Electrochemical generation of acid from low cost substrates (i.e. NaCl, seawater and weakly brine solutions and wastewater); and,
(2) Hydrometallurgical recovery of metals with electrochemically generated acid.

Here, we describe the electrochemical generation of acid from low cost substrates as well as the single stage and multistage leaching of LIB waste with the electrochemically generated acidic solutions under ambient conditions. Using electrolysis to generate the leaching solution from these low cost substrates has the potential to reduce the costs associated with leaching reagents and their regeneration, whilst also producing valuable secondary products, such as hydrogen gas, which can be a useful feedstock for other processes or as fuel. To our knowledge, this is the first study to assess the efficiency of leaching metals from LIB waste with an acidic anolyte solution generated by the electrolysis of salt or brine waters under ambient conditions.

2. Materials and methods

2.1. LIB waste preparation

Waste LIB from laptops of various manufacturers were obtained from a local WEEE processing facility (Total Green Recycling Ltd. Co., Perth, Western Australia), and manually dismantled to remove battery cells from plastic housings. The battery cells were then passed through a coarse shredder (Shredder Type 600, Kew), followed by milling (Essa LM5 mill). The crushed material was screened at 16 mm, 10 mm and 5 mm to remove oversized metal casings. Material smaller than 5 mm was re-milled. Size fractions below 500 μm were obtained and analysed for metal and carbon content. The sub 500 μm fraction was used for this study. The composition of the battery waste was examined by x-ray diffraction (XRD) and scanning electron microscopy by CSIRO Analytical Services Laboratory (Perth, Western Australia).

2.2. Natural pH and acid consumption of LIB waste

The natural pH of the LIB waste was determined by mixing 10% (w/v) crushed LIB waste with distilled water. The pH of the mixture was measured periodically using a TPS Smart-CHEM meter with pH-TPS double junction sensor (Ag/AgCl reference electrode) until the readings were stable.

The acid consuming nature of the LIB waste was assessed by determining the amount of protons (H^+) required to stabilise the pH of the 10% (w/v) slurry at a set value. The set pH values tested were pH 1, 2, 3, 4, and 5. These values were chosen to reflect limits for metal solubility of the major metals contained in the LIB waste (Al, Co, Mn, Ni, Cu and Li) as shown by their respective Pourbaix diagrams for pH and redox potential (AIST, 2005).

The mass of HCl consumed was measured over time at 4 h, 12 h and 24 h. Initially, 10% (w/v) LIB waste was suspended in 100 mL of ultrapure water. The suspension was equilibrated with slow speed magnetic stirring for 30 min prior to dosing of acid (4 M or concentrated HCl, depending on the set point). The pH and acid dosing were computer-controlled using LabVIEW (National Instruments). The pH was recorded using TPS Ionide pH probes (Ag/AgCl reference electrode) that were calibrated with pH 7.01 and 4.01 standard buffers. Acid was dosed at a fixed flow rate and time using a peristaltic pump (Masterflex). The volume of acid delivered was translated into the mass of HCl required to maintain the pH of the slurry at the set value. This acid consumption was expected to be proportional to the natural alkalinity of the LIB waste used for leaching experiments.

2.3. Production of acidic anolyte solution by electrolysis of 0.5 M sodium chloride solution

A laboratory-scale, two-chamber electrochemical cell was constructed with Perspex for the production of the acidic anolyte solution for leaching (Fig. 1). The electrochemical cell consisted of two identical half cells (internal dimensions: 14 cm × 12 cm × 2 cm) separated by a cation exchange membrane (Ultrex CMI-7000, Membrane International Inc.; surface area: 168 cm^2).

For initial experiments, both half cells were loaded with conductive graphite granules (KAIYU Industrial Ltd.; diameter: 3–5 mm; bulk density: 0.8 $kg\ L^{-1}$; surface area: $1.308 \pm 0.003\ m^2\ g^{-1}$). The amount of granules loaded into each half cell was approximately 93 g, giving an estimated surface area of approximately 121 m^2. The void volume in each half cell was reduced from 336 mL to 220 mL. Four graphite rod electrodes (KAIYU Industrial Ltd; diameter: 5 mm; length: 12 cm) were used as current collectors. Additional experiments were conducted with a mixed metal oxide-coated titanium (MMO-Ti) anode mesh and a titanium cathode mesh (NMT Electrodes (Australia) Pty Ltd.; Western Australia). Both electrode meshes had an identical dimension (12.5 cm × 12 cm × 0.1 cm; estimated surface area 225 cm^2). A titanium rod (diameter 5 mm) was welded to each mesh to enable electrical contact with the external circuit of the electrochemical cell.

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