Available online at www.sciencedirect.com
ScienceDirect
Hydrometallurgy 84 (2006) 75–80
hydrometallurgy
www.elsevier.com/locate/hydromet

Recovery of metal values from a mixture of spent lithium-ion batteries and nickel-metal hydride batteries

Junmin Nan *, Dongmei Han, Minjie Yang, Ming Cui, Xianlu Hou

School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

Received 18 November 2005; received in revised form 5 January 2006; accepted 27 March 2006
Available online 3 July 2006

Abstract

A novel process for the recovery of metal values from a mixture of spent lithium-ion batteries (LIBs) and nickel-metal hydride (NiMH) batteries is presented. The iron shells of spent batteries were firstly dismantled using a specially designed dismantling machine. Then after the separation of aluminum substrate and electrolyte and the subsequent heating treatment, iron shells and metal-mesh substrate in the dismantled substances were effectively separated with a sieve. The powder residues including $LiCoO_2$, copper oxides, metal nickel and hydrogen storage alloy and their oxides were dissolved using 3 mol L^{-1} H_2SO_4+3 wt.% H_2O_2 at 70 °C, S/L = 1:15 for 5 h. Finally, rare earths (RE) were precipitated as sodium RE double sulfate, copper was extracted as $CuSO_4$ with 10 wt.% Acorga M5640 at pH = 1.5–1.7, cobalt and nickel were extracted as their sulfates with 1 M Cyanex272 at pH = 5.1–5.3 and 6.3–6.5, respectively. The experimental results showed that the recovery exceeded 94% for all metal values.

Keywords: Copper; Nickel; Cobalt recovery; Spent lithium-ion batteries; Spent nickel-metal hydride batteries; Solvent extraction

1. Introduction

Lithium-ion batteries (LIBs) and nickel-metal hydride (NiMH) batteries have played a leading role in the portable secondary battery market since their commercialization (Köhler et al., 2004; Nishi, 2001). Because metal values such as nickel, cobalt, copper and rare earths (La, Ce, Pr and Nd, shown as RE) and corrosive electrolytes are contained in both batteries, recycling of spent LIBs, and NiMH batteries has become an urgent matter from the viewpoint of environmental protection and resource conservation.

Up to now, some typical hydrometallurgical and pyrometallurgical processes for the recycling of spent LIBs and NiMH batteries have been reported or patented (Han and Nan, 2005; Espinosa et al., 2004); Co, Li and Cu are usually recovered from spent LIBs (Zhang et al., 1998a,b; Kim et al., 2004; Lin et al., 2003; Tanii et al., 2003), and Co, Ni and RE or Fe-based alloy are reclaimed from spent NiMH batteries (Kleinsorgen et al., 2000; Pietrelli et al., 2002; Zhang et al., 1999, 1998a,b). In these reported hydrometallurgical process, di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis-(2,4,4-tri-methyl-pentyl) phosphinic acid (Cyanex272), trioctylamine (TOA), diethylhexyl phosphoric acid (DEHPA) or 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) were usually used as extractants to separate the metal values. In addition, using spent batteries to prepare $LiCoO_2$ electrode materials (Lee and Rhee, 2003; Contestabile et al.,

---

* Corresponding author. Tel.: +86 20 39310255; fax: +86 20 39310187.
E-mail address: jmnan@scnu.edu.cn (J. Nan).

0304-386X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.hydromet.2006.03.059

2001; Nan et al., 2004), metal hydride electrodes (Wang et al., 2002; Prickett et al., 2001) and Ni–Co alloy (Lupi and Pilone, 2002) were also investigated.

Based on hydrometallurgical processes, we investigated methods for recycling spent LIBs and spent NiMH batteries, and metal values and electrode materials including Co, Li, Ni, Cu, $LiCoO_2$ and $Ni(OH)_2$ were obtained (Nan et al., 2004, 2005, 2006). In the recycling process of spent LIBs (Nan et al., 2005), oxalate and Cyanex272 were employed to separate Co and subsequently synthesize $LiCoO_2$ electrode material, most copper was left as metal strip and the small amount of Cu dissolved with H_2SO_4 was extracted with Acorga M5640 (hydroxy-oxime derivative). In the recycling process of spent NiMH batteries (Nan et al., 2006), the recovered $NiSO_4+CoSO_4$ solution was employed to synthesize Ni $(OH)_2$ electrode material after the separation of outer shells, RE and impurities. However, it was also noticed that mixing of these two spent batteries was unavoidable during collection, and dealing with the separation of the mixed spent batteries was relatively difficult in the practical treatment process. Because more elements would be involved in the target batteries, and the cost and large-scale feasibility should also be particularly considered for a practicable process, those proposed processes that solely reclaimed spent LIBs or spent NiMH batteries were unusable for the combined spent batteries and thus must be readjusted.

Considering that metal values of Co and Cu and organic $LiPF_6$ electrolyte, and Ni, Co and RE and corrosive alkaline electrolyte are contained in LIBs and NiMH batteries, respectively, and some species such as their electrolytes can react with each other, a novel process was developed to reclaim a mixture of spent LIBs and NiMH batteries. In this paper, the pretreatment of spent batteries, and the recovery of metal values including RE, Co, Cu and Ni from a mixture of spent LIBs and NiMH batteries are all presented.

2. Experimental

2.1. Materials

The cylindrical spent LIBs and NiMH batteries used in this work were kindly provided by Great Power Battery Co. LTD. The positive electrodes of spent NiMH batteries were comprised of formed nickel substrate and $Ni(OH)_2$ active material, the negative electrodes consisted of AB_5-type hydrogen storage alloy powders and iron or copper-mesh substrate. In spent LIBs, $LiCoO_2$ and carbon powders were pasted on aluminum foil and copper foil as positive and negative electrodes, respectively. The contents of the substances in the two batteries were similar to those of the commercial batteries with the same size in the market.

A half of spent LIBs and NiMH batteries were used. The commercial extractions Acorga M5640 and Cyanex272 (di-(2,4,4 trimethyl pentyl) phosphoric acid) were used as extractants for the separation of Cu^{2+}, Ni^{2+} and Co^{2+}. Kerosene was used as diluent both for Acorga M5640 and Cyanex272. All reagents were utilized as-received without further purification.

2.2. Analysis methods

The concentrations of various metallic ions in the initial solutions and subsequent resultants were all determined by using atomic absorption spectrophotometer (model AA320, China). The pH values of the aqueous solutions were measured with a pH/mV meter (Model DF-801, China).

3. Results and discussion

3.1. Separation of the outer iron shells of spent batteries

The desirable metal values, i.e. Ni, Cu, Co and RE, were contained in the inner part of spent batteries, in order to separate these elements out, respectively, the outer iron shells of spent batteries must be firstly dismantled and separated. An especially designed dismantling machine was used to accomplish this. The digital image of the dismantled substances is shown in Fig. 1a. It can be seen that the inner substances of spent batteries were peeled off after the dismantling of battery shells, which is very usable to the next separating treatment.

It was found that self-ignition of the dismantled substance occurred easily due to the short circuit of two electrodes and the contact of hydrogen storage alloy powders with moist air. In addition, the electrolyte of spent LIBs, i.e. lithium phosphohexafluoride ($LiPF_6$) dissolved in organic solvent, could also react with water and produce dangerous gases such as pentafluoroarsenic, pentafluorophosphate and hydrogen fluoride. So, the dismantled substances were immediately poured into a plastic container with alkaline solution after the dismantling treatment. The electrolyte of NiMH batteries is corrosive alkaline solution, while an acidic solution is produced from LIBs when its organic electrolyte contacted with water. Because the alkaline solution had a high concentration, some alkaline solution would be left after the acid–base neutralization reaction, thus, some of the aluminum substrates of LIBs could also be dissolved. The recovery value of aluminum is negligible, and the introduction of Al^{3+} in the next dissolving step would go against the separation of metal values (Nan