



Recycling of lithium-ion batteries: a novel method to separate coating and foil of electrodes



Christian Hanisch^{a, b, *}, Thomas Loellhoeffel^a, Jan Diekmann^{a, b}, Kely Jo Markley^{a, c}, Wolfgang Haselrieder^{a, b}, Arno Kwade^{a, b}

^a Institute for Particle Technology, TU Braunschweig, Volkmaroder Str. 5, 38104, Braunschweig, Germany

^b Lion Engineering GmbH, Rebenring 33, 38106, Braunschweig, Germany

^c University of Mississippi, P.O. Box 1848, Oxford, MS, 38677, USA

ARTICLE INFO

Article history:

Received 9 June 2015

Received in revised form

4 August 2015

Accepted 6 August 2015

Available online 15 August 2015

Keywords:

Lithium-ion batteries

Recycling

Recovering

Electrodes

Scraps

Active materials

ABSTRACT

Lithium-ion batteries will play a crucial role in the development of mobile consumer devices, stationary energy storage systems, and electric mobility. The growth in these fields will bring about a surge in the lithium-ion battery market. This leads experts to agree that more effective recycling processes are needed in conjunction with the recycling of lithium. This calls for an entirely revolutionary recycling process which we here have attempted to develop.

Our approach uses thermal decomposition of the polyvinylidene fluoride binder to lessen the cohesion of coated active material particles and weaken the adhesion between coating and foil. Then, an air-jet-separator is able to detach the coating powder from the current collector foils while stressing remaining particulate agglomerates. This separation process named ANVIL (Adhesion Neutralization via Incineration and Impact Liberation) was tested on a laboratory scale with electrode rejects. We compared this to the widely used mechanical recycling process that utilizes a cutting mill to separate the current collector and coating. Intermediates and products were characterized using thermogravimetric analysis, tape adhesion tests, atomic absorption spectroscopy, particle size analysis, and gravimetric sieve analysis. We found that 97.1% w/w of the electrode coating can be regained with aluminum impurities of only 0.1% w/w, 30 times purer than the comparative process. This demonstrates a more effective recycling process than is currently available that also enables the recapture of lithium from the electrode coating.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The transition from combustion engines to electric vehicles is one highly pursued path in the effort to reduce oil consumption. Electric mobility can also reduce overall energy consumption if it is applied as part of a bigger transition to a more sustainable economy (Bauer et al., 2015; van Vliet et al., 2011). Battery-powered support in hybrid vehicles will enable the use of high-efficiency technology that combustion engines cannot adopt on their own such as regenerative braking (Lv et al., 2015) and electrical driving in slow city or traffic jam situations (Lee et al., 2013). Furthermore, electric vehicles (EV) can contribute to the overall reduction of air pollution in mega-cities (Bauer et al., 2015; Baumann et al., 2012). The

demand for lithium ion batteries (LIBs) is expected to rise even further in the field of portable electronics as well as stationary energy storage as LIBs will play a substantial role in enabling the efficient use of renewable energy sources (Hammond and Hazeldine, 2015; Scrosati and Garche, 2010). In all fields, electrochemical storage technology – predominantly lithium ion batteries – determine the lifetime of some products or are the component which has to be replaced first. These factors will lead to a growing demand in spent battery collection systems (Sun et al., 2015) and recycling technologies for electrochemical storage devices (Hanisch et al., 2015a; Hoyer et al., 2014; Richa et al., 2014; Zeng and Li, 2014; Ziemann et al., 2013).

1.1. Need for recycling

Recent research states that the demand of cobalt for the production of 20 million EV batteries per year – with averaged recent

* Corresponding author. Institute for Particle Technology, Volkmaroder Str. 5, 38118, Braunschweig, Germany. Tel.: +49 531 391 94656; fax: +49 351 3919633.
E-mail address: c.hanisch@tu-braunschweig.de (C. Hanisch).

material compositions – would be about equal to current world mine production of cobalt and would deplete current cobalt reserves in less than 60 years. The nickel needed for the production of 20 million EV batteries per year would be larger by 170 fold than today's existing production capacity (Delucchi et al., 2014). These figures alone signify a need for an alternative method of resource acquisition. The recycling of products containing Ni and Co has already shown benefits in terms of scarce and expensive material conservation as well as in the reduction of material production emissions like SO_x (Sullivan and Gaines, 2012). Energy consumption during lithium-ion battery production can be reduced due to the use of recycled materials (Simon and Weil, 2013; Sullivan and Gaines, 2012). Additionally, in-production recycling of active materials can result in substantial economic and ecological savings (Hanisch et al., 2015b).

However nowadays, recycling processes focus on the recycling of cobalt and nickel, not lithium. This is related to the higher raw material costs of these transition metals compared with the costs of the less expensive lithium (Dunn et al., 2012; Ziemann et al., 2012). No real lithium scarcity is foreseen until 2050 when easily extractable reserves in stable countries could decrease significantly (Weil and Ziemann, 2014). Recent debates often conclude that there is sufficient lithium available in terms of resources, but the potential increase in the production rate has yet to be properly regarded. Lithium resources, excluding the lithium in the oceans, are calculated at 30 Mt (Kushnir and Sandén, 2012) or 38.68 Mt (Gruber et al., 2011). Thus, Lithium will only be in critical supply within this century if EV batteries become used on large scale "or if batteries are not recycled" (Kushnir and Sandén, 2012) with recycling rates of at least 90% (Gruber et al., 2011). A substantial potential for lithium recycling is seen in Europe (Miedema and Moll, 2013), in China (Zeng and Li, 2013) and in the United States (Wang et al., 2014). All aforementioned experts agree on the necessity of lithium recycling for long-term sustainability.

1.2. Recycling of lithium-ion batteries – state of the art

Long and diverse process chains have to be applied to recycle lithium-ion batteries efficiently especially in the case of those from electric vehicles (Hanisch et al., 2015a):

First, a deactivation step can lower the dangers resulting from the stored energy and chemical reaction potential of charged lithium-ion batteries. The batteries should be discharged to minimize the stored energy. Thermal pretreatment steps then can be used to volatilize the electrolyte or even to decompose all organic compounds of the battery cells (Georgi-Maschler, 2009; Vezzini, 2014a). Alternatively, lithium-ion batteries could be frozen thus inactivating the galvanic elements. The temperature of all flammable components is reduced far below their flashing points so that an ignition is prevented.

Bigger battery systems (e.g. from electric vehicles) can be disassembled to decrease the size and remaining electrochemically stored energy. At present, the variety of battery system designs is wide due to a low degree of standardization. Consequently, manual disassembly steps are usually employed (Herrmann et al., 2014).

In most cases, the next step of the recycling process is crushing. The battery cells are opened and valuable components of the cells are released. Dry and wet crushing operations can be applied (Zhang et al., 2013a).

The resulting fragments of electrodes, separator, case, and a powder fraction consisting of coating agglomerates have to be separated for further recycling. This can be accomplished with a combination of sorting and sieving steps such as magnetic separation and air separation methods like cross-flow classification or zigzag sifting (Hanisch et al., 2015a).

A more intensive, second milling step then can be applied to remove the remaining particulate coating from the current collector foil. This increases the yield of coating fragments and foil with fewer impurities in each of the fractions (Hanisch et al., 2011a). Due to the fact that the mechanical stressing not only loosens the coating from the foil but also results in some smaller foil fragments, these fragments have to be screened.

Alternatively, other mechanisms such as dissolving the binder in a solvent (Contestabile et al., 2001; Hanisch et al., 2011b, 2015b; Li et al., 2009c; Li et al., 2013) or decomposing the binder under high temperatures (Hanisch et al., 2013, 2014) work to separate the current collector and the particulate coating.

In this work, a combination of thermal and mechanical processes is used to separate current collector foil and coating. Depending on the binder chemistry the electrode compound is heated up to 400–800 °C and the binder (mostly polyvinylidene fluoride) decomposes releasing hydrogen fluoride and other gaseous components. A vacuum pyrolysis at 600 °C with a pressure below 1 kPa for 30 min can be used to evaporate organic components (Sun and Qiu, 2011). Other processes using thermal decomposition of the binder components are discussed in literature (Gu and Nie, 2011; Lee and Rhee, 2002; Li et al., 2009c, 2013; Lu et al., 2013; Song et al., 2013; Sun and Qiu, 2011, 2012).

The regained powder fraction still contains all of the components of the original coating: the desired lithium-rich battery active material, graphite, conductive carbon, binder, and even some components from the electrolyte – like organic residues such as ethylene carbonate, dimethyl carbonate, and conductivity salt. In the event of a previous thermal decomposition, the organic fractions and conductivity salt would have already reacted.

Metallurgical processes have to be applied in order to regain the valuable metals cobalt, nickel and lithium from the former-coating powder. In pyro-metallurgical processes several components of battery cells or the battery cells themselves are melted. The transition metals nickel, cobalt, and copper can be recycled from the cast while lithium and aluminum remain in the slag. Copper, cobalt, and nickel can be regained after further processing of smelter output via leaching and solvent extraction. 98% w/w of cobalt and 93% w/w nickel can be recovered pyro-metallurgically (Swart et al., 2014). Due to the fact that pyro-metallurgical recovery of lithium and aluminum is currently not possible from pyro-metallurgical processes, further treatment is necessary to recover lithium (Elwert et al., 2012; Georgi-Maschler et al., 2012; Li et al., 2013).

Alternatively or additionally to pyro-metallurgy hydro-metallurgical processes can be applied. These processes like leaching, extraction, crystallization and precipitation are needed to recover pure metals, e.g. lithium, from separated coating materials or from slag of pyro-metallurgical processes.

Furthermore, products of the hydrometallurgical processes can be used to re-synthesize battery active materials in battery grade. More comprehensive reviews on hydro-metallurgical processes in the field of recycling of lithium-ion batteries are reviewed in literature (Chagnes and Pospiech, 2013; Hanisch et al., 2015a; Joulíé et al., 2014) and included in general reviews about lithium-ion battery recycling (Xu et al., 2008; Zeng et al., 2014; Zhang et al., 2013b). The first step of a hydro-metallurgical treatment is the leaching of the regained powder fractions including the active material fraction. In this process, the lithium-transition metal compounds are leached in inorganic or organic acids in order to prepare them for the later separation steps. The reduction of impurities and organic residues as well as the separation of the different product metals as purely as possible are the goals of the leaching process step. Nitric acid (HNO₃) can be used with the addition of hydrogen peroxide (H₂O₂) to leach LiCoO₂ (Lee and Rhee, 2002) as well as sulfuric acid (H₂SO₄), hydrochloric acid

Download English Version:

<https://daneshyari.com/en/article/10688164>

Download Persian Version:

<https://daneshyari.com/article/10688164>

[Daneshyari.com](https://daneshyari.com)